Electronic Supplementary Information

Enantioselective Synthesis of 2-Substituted and 3-Substituted Piperidines through a Bromoaminocyclization Process

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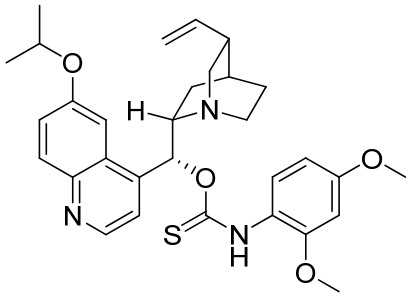
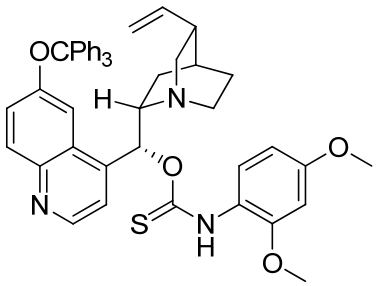
(A) General. All reactions that required anhydrous conditions were carried by standard procedures under nitrogen atmosphere. Commercially available reagents were used as received. The solvents were dried by distillation over the appropriate drying reagents. Infrared spectra were recorded on a BIO-RAD FTS 165 FT-IR spectrophotometer and reported in wave numbers (cm^{-1}). Melting points were determined on a BÜCHI B-540b melting point apparatus. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker ACF300 (300 MHz), Bruker DPX300 (300 MHz) or AMX500 (500 MHz) spectrometer. Chemical shifts (δ) are reported in ppm relative to TMS (δ 0.00) for the ^{1}H NMR and to chloroform (δ 77.0) for the ^{13}C NMR measurements. Low resolution mass spectra were obtained on a Finnigan/MAT LCQ spectrometer in ESI mode. High resolution mass spectra were obtained on a Finnigan/MAT 95XL-T spectrometer. Enantiomeric excesses were determined by HPLC analysis on Shimadzu HPLC units, including the following instruments: pump, LC-20AD; detector, SPD-20A; column, Daicel Chiralpak IA, IB or IC. Optical rotations were recorded on a Jasco DIP-1000 polarimeter. Analytical thin layer chromatography (TLC) was performed with Merck pre-coated TLC plates, silica gel 60F-254, layer thickness 0.25 mm. Flash chromatography separations were performed on Merk 60 (0.040-0.063 mm) mesh silica gel.

(B) Catalysts 6a-6n were synthesized according to the report procedure.[1]



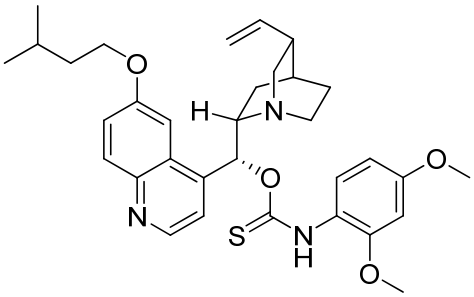
Amino-thiocabamate 6e

72%; light yellow solid, $[\alpha]_D^{28}$ +155.9 (*c* 1.0, CH_2Cl_2); IR (KBr): 2939, 1618, 1524, 1307, 1209, 1161 cm^{-1}; ^1H NMR (the compound existed as a mixture of rotamers and the major rotamer was assigned) (300 MHz, $CDCl_3$): δ 8.70 (d, *J* = 4.1 Hz, 1H), 8.50-8.45 (m, 1H), 7.98 (d, *J* = 9.1 Hz, 1H), 7.50-7.29 (m, 5H), 6.45 (s, 2H), 5.85-5.77 (m, 1H), 4.97-4.94 (m, 2H), 4.78-4.63 (m, 1H), 3.80 (s, 6H), 3.46-3.42 (m, 1H), 3.20-3.01 (m, 2H), 2.69-2.49 (m, 2H), 2.18-2.04 (m, 1H), 1.90-1.52 (m, 5H), 1.39 (d, *J* = 3.5 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 188.0, 158.6, 155.9, 151.9, 147.1, 144.5, 141.7, 131.5, 127.1, 124.6, 123.1, 122.9, 119.4, 118.9, 114.3, 103.9, 103.5, 98.7, 81.7, 70.0, 59.8, 56.6, 55.4, 42.5, 39.6, 27.5, 24.1, 21.8; HRMS (ESI) calcd for $C_{31}H_{38}N_3O_4S$ *m/z* $[M + H]^+$: 548.2578; found: 548.2597.



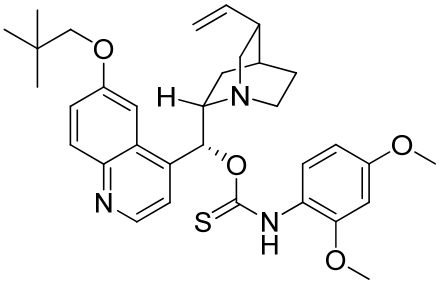
Amino-thiocabamate 6f

69%; light yellow solid, $[\alpha]_D^{28}$ +72.6 (*c* 1.0, CH_2Cl_2); IR (KBr): 2941, 1639, 1526, 1209, 1159, 1034 cm^{-1}; ^1H NMR (the compound existed as a mixture of rotamers and the major rotamer was assigned) (400 MHz, $CDCl_3$): δ 8.90 (brs, 1H), 8.71 (d, *J* = 4.5 Hz, 1H), 7.99 (d, *J* = 9.2 Hz, 1H), 7.48-7.28 (m, 5H), 6.43 (s, 2H), 5.79-5.72 (m, 1H), 4.97-4.94 (m, 2H), 3.77-3.62 (m, 8H), 3.41-3.39 (m, 1H), 3.13-3.01 (m, 2H), 2.67-2.57 (m, 2H), 2.28-2.15 (m, 1H), 1.84-1.42 (m, 5H), 1.07 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.2, 158.2, 154.6, 152.3, 147.8, 143.8, 141.9, 129.0, 127.9, 127.3, 126.3, 126.0, 114.2, 113.0, 103.9, 98.8, 91.2, 81.7, 60.0, 59.1, 55.5, 42.5, 42.2, 39.8, 27.7, 27.6, 24.1; HRMS (ESI) calcd for $C_{47}H_{46}N_3O_4S$ *m/z* $[M + H]^+$: 748.3204; found: 748.3231.



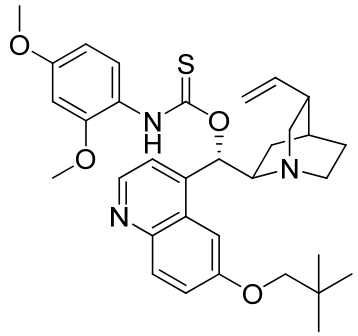
Amino-thiocabamate 6g

73%; light yellow solid, $[\alpha]_D^{28}$ +149.4 (*c* 1.6, CH_2Cl_2); IR (KBr): 2951, 1619, 1513, 462, 1209, 1160, 1034 cm^{-1}; ^1H NMR (the compound existed as a mixture of rotamers and the major rotamer was assigned) (400 MHz, $CDCl_3$): δ 8.71 (d, *J* = 4.3 Hz, 1H), 8.44 (br, 1H), 7.98 (d, *J* = 9.2 Hz, 1H), 7.64-7.31 (m, 5H), 6.47-6.44 (m, 2H), 5.83-5.77 (m, 1H), 5.00-4.95 (m, 2H), 4.16-4.01 (m, 2H), 3.86-3.68 (m, 6H), 3.45-3.42 (m, 1H), 3.14-2.99 (m, 2H), 2.62-2.56 (m, 2H), 2.24-2.15 (m, 1H), 1.92-1.43 (m, 8H), 0.99 (d, *J* = 6.5 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 188.1, 158.6, 157.3, 151.9, 147.2, 144.7, 143.0, 141.8, 131.5, 127.2, 124.6, 122.3, 119.4, 119.3, 114.3, 103.9, 103.4, 102.6, 98.7, 81.7, 66.8, 59.7, 56.5, 55.5, 42.5, 39.7, 37.8, 27.5, 25.1, 24.1, 22.6; HRMS (ESI) calcd for $C_{33}H_{42}N_3O_4S$ *m/z* $[M + H]^+$: 576.2891; found: 576.2935.



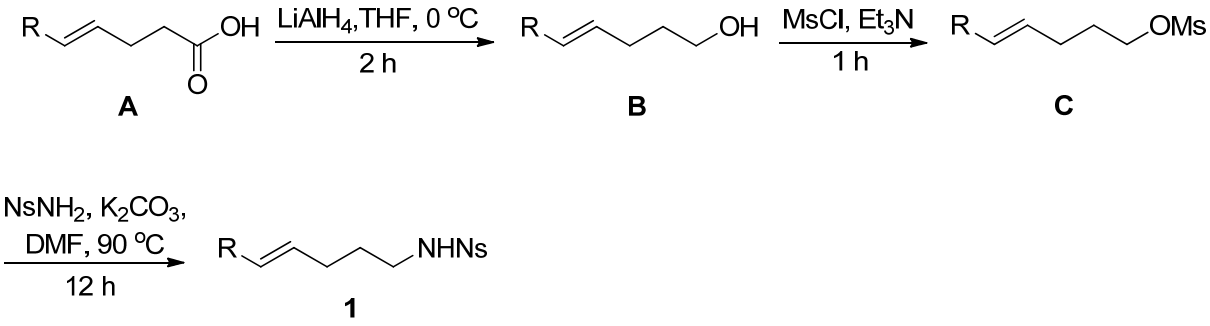
Amino-thiocabamate 6h

78%; light yellow solid, $[\alpha]_D^{28}$ +149.4 (*c* 1.6, CH_2Cl_2); IR (KBr): 2957, 1620, 1525, 1466, 1215, 1037 cm^{-1}; ^1H NMR (the compound existed as a mixture of rotamers and the major rotamer was assigned) (400 MHz, $CDCl_3$): δ 8.90 (brs, 1H), 8.71 (d, *J* = 4.5 Hz, 1H), 7.99 (d, *J* = 9.2 Hz, 1H), 7.48-7.28 (m, 5H), 6.43 (s, 2H), 5.79-5.72 (m, 1H), 4.97-4.94 (m, 2H), 3.77-3.62 (m, 8H), 3.41-3.39 (m, 1H), 3.13-3.01 (m, 2H), 2.67-2.57 (m, 2H), 2.28-2.15 (m, 1H), 1.84-1.42 (m, 5H), 1.07 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 188.0, 170.8, 158.6, 157.6, 152.3, 146.9, 144.4, 143.0, 141.5, 131.1, 126.8, 125.1, 122.1, 119.1, 114.1, 103.8, 102.4, 98.6, 81.2, 78.0, 60.1, 59.2, 56.3, 55.2, 42.4, 39.4, 31.7, 27.3, 26.4, 23.6; HRMS (ESI) calcd for $C_{33}H_{42}N_3O_4S$ *m/z* $[M + H]^+$: 576.2891; found: 576.2913.



Amino-thiocabamate 6i

75%; light yellow solid, $[\alpha]_D^{28}$ –150.2 (*c* 0.9, CH_2Cl_2); IR (KBr): 2953, 1620, 1525, 1463, 1209, 1036 cm^{-1}; ^1H NMR (the compound existed as a mixture of rotamers and the major rotamer was assigned) (300 MHz, $CDCl_3$): δ 8.76-8.72 (m, 2H), 8.00 (d, *J* = 9.2 Hz, 1H), 7.62-7.56 (m, 1H), 7.41-7.30 (m, 4H), 6.54-6.44 (m, 2H), 6.13-5.92 (m, 1H), 5.25-5.06 (m, 2H), 3.81-3.67 (m, 8H), 3.42-3.39 (m, 1H), 2.92-2.76 (m, 4H), 2.26-2.00 (m, 2H), 1.81-1.77 (m, 1H), 1.56-1.52 (m, 3H), 1.10 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 187.9, 157.6, 151.6, 147.0, 144.4, 143.4, 140.2, 131.1, 127.3, 124.3, 123.4, 122.2, 119.3, 118.4, 114.5, 103.8, 102.5, 98.6, 80.4, 78.0, 60.1, 59.7, 55.3, 49.1, 40.0, 31.7, 27.8, 26.5, 26.2, 24.0; HRMS (ESI) calcd for $C_{33}H_{42}N_3O_4S$ *m/z* $[M + H]^+$: 576.2891; found: 576.2903.

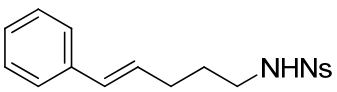


(C) General procedure for the preparation of olefinic amide 1

To a solution of acid **A** (1.0 mmol, 1.0 eq) (synthesized according to the literature procedure[3]) in THF (10 mL) was added $LiAlH_4$ (76 mg, 2.0 mmol, 2.0 eq) at 0 °C under N_2. The resulting mixture was stirred at 0 °C for 10 min and then was warmed to 25 °C and stirred for another 3 h. After TLC revealed the absence of the starting material, the reaction was quenched with crushed ice. The mixture was filtered through a thin pad of silica gel and eluted with EtOAc (20 mL). The filtrate was concentrated *in vacuo*, which was used directly without further purification, or purified by a short column (hexane/EtOAc 3:1) to give alcohol **B**.

To a solution of alcohol **B** (1.0 mmol, 1.0 eq) and triethylamine (418 μL, 3.0 mmol, 3.0 eq) in CH_2Cl_2 (5 mL) was added MsCl (116 μL, 1.5 mmol, 1.5 eq) at 0 °C. The resulting mixture was stirred at 0 °C for 10 min and then was warmed to 25 °C and stirred for another 2 h. After TLC revealed the absence of the starting material, the reaction was quenched with water (4 mL) and extracted with CH_2Cl_2 (3 × 5 mL). The combined organic extracts were dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash column chromatography (hexane/EtOAc 3:1) to give the compound **C**.

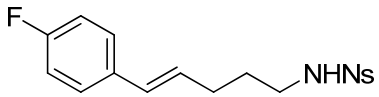
A modified literature[2] procedure was used for the direct conversion of Ms-activated alcohols to the corresponding 4-nitrobenzenesulfonamides. A solution of compound **C** (1.0 mmol, 1.0 eq), $NsNH_2$ (404 mg, 2.0 mmol, 2.0 eq) and K_2CO_3 (276 mg, 2.0 mmol, 2.0 eq) in DMF (5 mL) was stirred at 90 °C for 12 h. The reaction mixture was diluted with water (10 mL) and extracted with Et_2O (3 × 15 mL). The combined organic extracts were washed with water (3 × 10 mL) and brine, dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash column chromatography (CH_2Cl_2/hexane 2:1 to pure CH_2Cl_2) to give the product **1**.



(*E*)-4-Nitro-*N*-(5-phenylpent-4-enyl)benzenesulfonamide (1a)

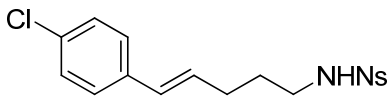
Yellow solid, IR (KBr): 3259, 3103, 1546, 1350, 1160, 1061 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 8.30 (d, J = 8.8 Hz, 2H), 8.05 (d, J = 9.0 Hz, 2H), 7.29-7.19 (m, 5H), 6.34 (d, J = 15.8 Hz, 1H), 6.08 (dt, J = 15.8, 6.9 Hz, 1H), 5.18 (t, J = 5.8 Hz, 1H), 3.06 (dt, J = 6.7 Hz, 2H), 2.23 (dt, J = 6.9 Hz, 2H), 1.74-1.65 (m,

2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 149.9, 145.7, 137.0, 131.1, 128.5, 128.4, 128.2, 127.2, 125.8, 124.3, 42.6, 29.6, 29.0; HRMS (ESI) calcd for $C_{17}H_{17}N_2O_4S$ *m/z* $[M - H]^-$: 345.0915; found: 345.0920.



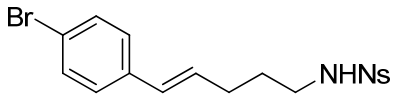
(*E*)-N-[5-(4-Fluorophenyl)pent-4-enyl]-4-nitrobezenesulfonamide (1b)

Yellow solid, IR (KBr): 3258, 1531, 1351, 1307, 1162, 1091 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.32 (d, *J* = 8.2 Hz, 2H), 8.05 (d, *J* = 8.5 Hz, 2H), 7.23 (dd, *J* = 8.2, 5.7 Hz, 2H), 6.96 (dd, *J* = 8.5 Hz, 2H), 6.29 (d, *J* = 15.8 Hz, 1H), 5.98 (dt, *J* = 15.1, 6.9 Hz, 1H), 5.06 (t, *J* = 5.8 Hz, 1H), 3.06 (dt, *J* = 6.3 Hz, 2H), 2.21 (dt, *J* = 7.0 Hz, 2H), 1.71-1.65 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 162.0 (d, *J* = 245.0 Hz), 150.0, 145.8, 133.3 (d, *J* = 3.6 Hz), 130.0, 128.2, 128.2 (d, *J* = 1.8 Hz), 127.3 (d, *J* = 7.3 Hz), 124.4, 115.4 (d, *J* = 21.9 Hz), 42.7, 29.6, 29.1; HRMS (ESI) calcd for $C_{17}H_{16}FN_2O_4S$ *m/z* $[M - H]^-$: 363.0820; found: 363.0813.



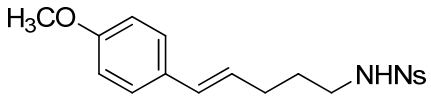
(*E*)-N-[5-(4-Chlorophenyl)pent-4-enyl]-4-nitrobezenesulfonamide (1c)

Yellow solid, IR (KBr): 3278, 1530, 1350, 1314, 1164, 1088 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.34 (d, *J* = 8.8 Hz, 2H), 8.04 (d, *J* = 8.8, Hz, 2H), 7.25 (d, *J* = 8.6 Hz, 2H), 7.21 (d, *J* = 8.6 Hz, 2H), 6.30 (d, *J* = 15.8 Hz, 1H), 6.07 (dt, *J* = 15.8, 6.9 Hz, 1H), 4.69 (t, *J* = 6.0 Hz, 1H), 3.08 (dt, *J* = 6.9 Hz, 2H), 2.23 (dt, *J* = 6.4 Hz, 2H), 1.73-1.58 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.1, 145.9, 135.6, 132.9, 130.2, 129.1, 128.7, 128.3, 127.2, 124.4, 42.8, 29.7, 29.2; HRMS (ESI) calcd for $C_{17}H_{16}ClN_2O_4S$ *m/z* $[M - H]^-$: 379.0525; found: 379.0516.



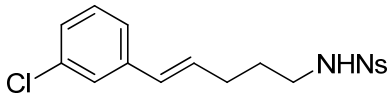
(*E*)-N-[5-(4-Bromophenyl)pent-4-enyl]-4-nitrobezenesulfonamide (1d)

Yellow solid, IR (KBr): 3279, 1529, 1412, 1349, 1163, 1050 cm^{-1}; ^{1}H NMR (300 MHz, Acetone-d_6): δ 8.42 (dd, *J* = 9.0 Hz, 2H), 8.13 (d, *J* = 9.0 Hz, 2H), 7.45 (d, *J* = 8.5 Hz, 2H), 7.30 (d, *J* = 8.5 Hz, 2H), 6.90 (brs, 1H), 6.37 (d, *J* = 16.1 Hz, 1H), 6.26 (dt, *J* = 15.8, 6.3 Hz, 1H), 3.06 (dt, *J* = 6.8 Hz, 2H), 2.24 (dt, *J* = 7.1 Hz, 2H), 1.74-1.65 (m, 2H); ^{13}C NMR (125 MHz, Acetone-d_6): δ 149.8, 146.6, 136.7, 131.2, 130.3, 129.1, 128.1, 127.5, 124.1, 119.8, 42.2, 29.5, 29.0; HRMS (ESI) calcd for $C_{17}H_{16}BrN_2O_4S$ *m/z* $[M - H]^-$: 423.0020; found: 423.0016.



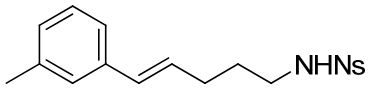
(*E*)-*N*-[5-(4-methoxyphenyl)pent-4-enyl]-4-nitrobenzenesulfonamide (1e)

Yellow solid, IR (KBr): 3282, 1529, 1349, 1240, 1165, 1041 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 8.31 (d, *J* = 9.0 Hz, 2H), 7.83 (d, *J* = 9.0 Hz, 2H), 7.22-7.17 (m, 2H), 6.82 (dd, *J* = 6.8, 2.0 Hz, 2H), 6.26 (d, *J* = 15.8 Hz, 1H), 5.91 (dt, *J* = 15.6, 6.9 Hz, 1H), 4.91 (t, *J* = 6.0 Hz, 1H), 3.80 (s, 3H), 3.05 (dt, *J* = 6.9 Hz, 2H), 2.20 (dt, *J* = 7.0 Hz, 2H), 1.72-1.62 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.9, 150.0, 145.8, 130.6, 128.2, 127.0, 126.1, 126.0, 124.3, 113.9, 55.3, 42.6, 29.7, 29.2; HRMS (ESI) calcd for $C_{18}H_{19}N_2O_5S$ *m/z* $[M - H]^-$: 375.1020; found: 375.1018.



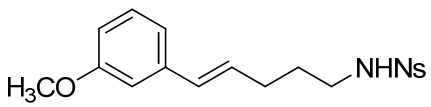
(*E*)-N-[5-(3-Chlorophenyl)pent-4-enyl]-4-nitrobezenesulfonamide (1f)

Yellow solid, IR (KBr): 32608, 1534, 1351, 1310, 1160, 1091 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.29 (d, *J* = 8.9 Hz, 2H), 8.01 (d, *J* = 9.0 Hz, 2H), 7.23-7.08 (m, 4H), 6.24 (d, *J* = 15.9 Hz, 1H), 6.05 (dt, *J* = 15.8, 6.9 Hz, 1H), 4.97 (t, *J* = 6.1 Hz, 1H), 3.02 (dt, *J* = 6.9 Hz, 2H), 2.19 (dt, *J* = 7.3, 1.2 Hz, 2H), 1.69-1.61 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.0, 145.8, 139.0, 134.4, 130.0, 129.9, 129.7, 128.2, 127.1, 125.8, 124.4, 124.2, 42.6, 29.6, 29.0; HRMS (ESI) calcd for $C_{17}H_{16}ClN_2O_4S$ *m/z* $[M - H]^-$: 379.0525; found: 379.0529.



(*E*)-4-Nitro-*N*-(5-*m*-tolylpent-4-enyl)benzenesulfonamide (1g)

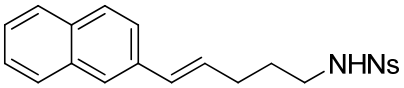
Yellow solid, IR (KBr): 3280, 1530, 1413, 1351, 1162, 1049 cm^{-1};^1H NMR (400 MHz, $CDCl_3$): δ 8.30 (d, *J* = 9.0 Hz, 2H), 8.04 (d, *J* = 9.0 Hz, 2H), 7.17 (d, *J* =7.5 Hz, 1H), 7.09-7.02 (m, 3H), 6.29 (d, *J* = 15.8 Hz, 1H), 6.06 (dt, *J* = 15.8, 6.9 Hz, 1H), 5.17 (t, *J* = 6.0 Hz, 1H), 3.06 (dt, *J* = 6.9 Hz, 2H), 2.33 (s, 3H), 2.22 (dt, *J* = 6.4, 1.1 Hz, 2H), 1.70-1.67 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.9, 145.7, 138.0, 137.0, 131.2, 128.4, 128.2, 128.1, 128.0, 126.6, 124.3, 123.0, 42.6, 29.6, 29.0, 21.3; HRMS (ESI) calcd for $C_{18}H_{19}N_2O_4S$ *m/z* $[M - H]^-$: 359.1071; found: 359.1076.



(*E*)-*N*-[5-(4-methoxyphenyl)pent-4-enyl]-4-nitrobenzenesulfonamide (1h)

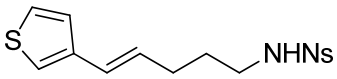
Yellow solid, IR (KBr): 3264, 1533, 1349, 1162, 1090 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 8.31 (d, *J* = 8.9 Hz, 2H), 8.03 (d, *J* = 9.0 Hz, 2H), 7.20 (dd, *J* = 7.7 Hz, 1H), 6.88-6.74 (m, 3H), 6.30 (d, *J* = 15.9 Hz,

1H), 6.06 (dt, *J* = 15.7, 6.9 Hz, 1H), 4.97 (t, *J* = 6.1 Hz, 1H), 3.80 (s, 3H), 3.05 (dt, *J* = 6.9 Hz, 2H), 2.22 (dt, *J* = 6.9 Hz, 2H), 1.73-1.63 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.7, 150.0, 145.8, 138.5, 131.1, 129.5, 128.7, 128.2, 124.4, 118.6, 112.6, 111.5, 55.2, 42.6, 29.6, 29.0; HRMS (ESI) calcd for $C_{18}H_{19}N_2O_5S$ *m/z* $[M - H]^-$: 375.1020; found: 375.1012.



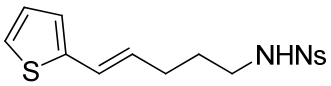
(*E*)-*N*-[5-(naphthalen-2-yl)-pent-4-enyl]-4-nitrobenzenesulfonamide (1i)

Yellow solid, IR (KBr): 3255, 1532, 1349, 1309, 1159, 1061 cm^{-1}; δ ^{1}H NMR (300 MHz, Acetone-d_6): δ 8.42 (d, *J* = 8.9 Hz, 2H), 8.15 (d, *J* = 8.9 Hz, 2H), 7.84-7.79 (m, 3H), 7.72 (s, 1H), 7.61 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.50-7.40 (m, 2H), 6.92 (t, *J* = 5.6 Hz, 1H), 6.56 (d, *J* = 15.8 Hz, 1H), 6.37 (dt, *J* = 15.8, 6.9 Hz, 1H), 3.10 (dt, *J* = 6.8 Hz, 2H), 2.30 (dt, *J* = 6.9 Hz, 2H), 1.78-1.68 (m, 2H); ^{13}C NMR (75 MHz, Acetone-d_6): δ 149.8, 146.6, 135.0, 133.6, 132.6, 130.5, 129.7, 128.1, 127.8, 127.6, 127.4, 126.0, 125.4, 125.2, 124.2, 123.2, 42.3, 29.5, 29.0; HRMS (ESI) calcd for $C_{21}H_{19}N_2O_4S$ *m/z* $[M - H]^-$: 395.1071; found: 395.1078.



(*E*)-4-nitro-*N*-[5-(thiophen-3-yl)pent-4-enyl]benzenesulfonamide (1j)

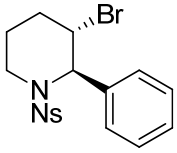
Yellow solid, IR (KBr): 3254, 1546, 1349, 1159, 1063, 967 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.28 (d, *J* = 8.9 Hz, 2H), 8.00 (d, *J* = 9.0 Hz, 2H), 7.22-7.19 (m, 1H), 7.07 (dd, *J* = 4.9, 1.0 Hz, 1H), 6.99 (dd, *J* = 3.0, 1.1 Hz, 1H), 6.30 (d, *J* = 15.8 Hz, 1H), 5.88 (dt, *J* = 15.8, 6.9 Hz, 1H), 4.98 (t, *J* = 6.1 Hz, 1H), 3.01 (dt, *J* = 6.9 Hz, 2H), 2.15 (ddd, *J* = 8.4, 7.2, 1.3 Hz, 2H), 1.69-1.58 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 150.0, 145.8, 139.7, 128.3, 128.2, 126.0, 125.5, 124.7, 124.4, 121.0, 42.6, 29.5, 29.1; HRMS (ESI) calcd for $C_{15}H_{15}N_2O_4S_2$ *m/z* $[M - H]^-$: 351.0479; found: 351.0461.



(*E*)-4-nitro-*N*-[5-(thiophen-2-yl)pent-4-enyl]benzenesulfonamide (1k)

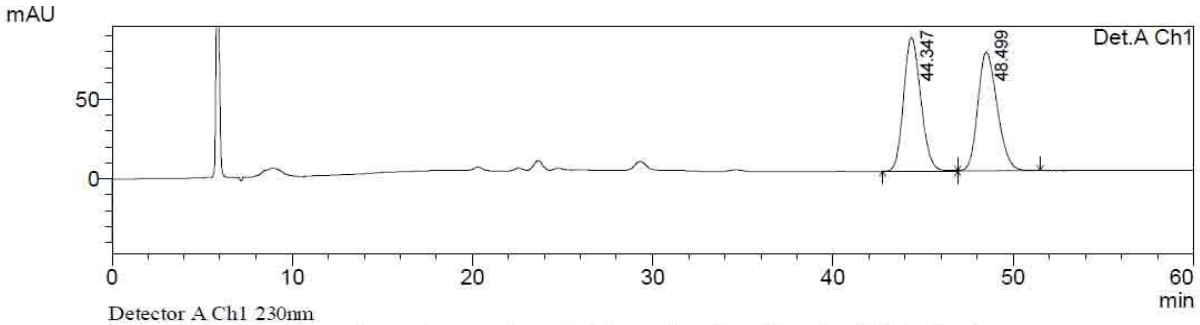
Yellow solid, IR (KBr): 3249, 1531, 1348, 1310, 1159, 1065 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.33 (d, *J* = 9.0 Hz, 2H), 8.04 (d, *J* = 9.1 Hz, 2H), 7.10 (d, *J* = 5.1 Hz, 1H), 6.92 (dd, *J* = 5.1, 3.5 Hz, 1H), 6.83 (d, *J* = 3.3 Hz, 1H), 6.45 (d, *J* = 15.6 Hz, 1H), 5.89 (dt, *J* = 15.6, 7.1 Hz, 1H), 4.86 (t, *J* = 5.8 Hz, 1H), 3.05 (dt, *J* = 6.7 Hz, 2H), 2.19 (ddd, *J* = 8.4, 7.1, 1.1 Hz, 2H), 1.72-1.62 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.0, 145.8, 142.2, 128.3, 128.2, 127.3, 124.8, 124.5, 124.4, 123.6, 42.6, 29.5, 29.0; HRMS (ESI) calcd for $C_{15}H_{15}N_2O_4S_2$ *m/z* $[M - H]^-$: 351.0479; found: 351.0461.

(D) General Procedure for the Bromoamidation. To a solution of olefinic amide **1** (0.1 mmol, 1.0 equiv), catalyst **6h** (0.01 mmol, 0.1 equiv) in the corresponding solvent (0.02 M) at corresponding temperature in dark under N_2 was added brominating source (0.12 mmol, 1.2 equiv). The resulting mixture was stirred at that temperature and monitored by TLC. The reaction was quenched with saturated Na_2SO_3 (2.0 mL) and then was warmed to 25 °C. The solution was diluted with water (3.0 mL) and extracted with CH_2Cl_2 (3 × 5 mL). The combined extracts were washed with brine (5.0 mL), dried ($MgSO_4$), filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel (CH_2Cl_2/hexane 2:1) to yield the corresponding piperidine **2**.



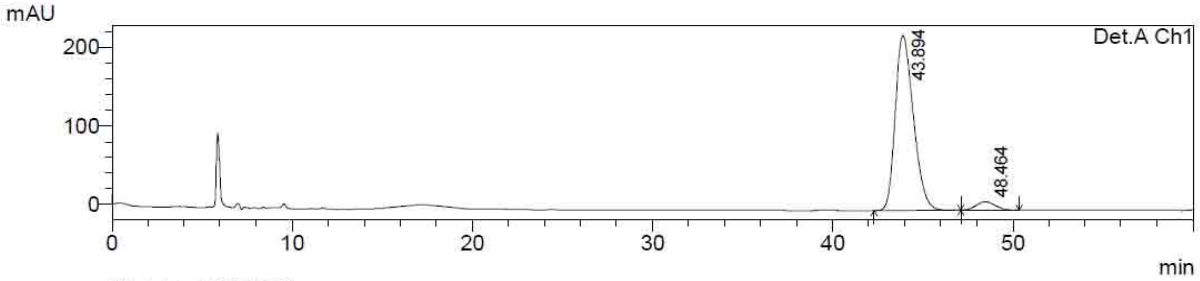
(2*S*,3*R*)-3-Bromo-1-(4-nitrophenylsulfonyl)-2-phenylpiperidine (2a)

White solid, $[\alpha]_D^{26}$ –17.6 (*c* 1.4, CH_2Cl_2, 90% ee); IR (KBr): 2939, 1526, 1349, 1312, 1160, 1108 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 8.31 (d, *J* = 8.8 Hz, 2H), 8.06 (d, *J* = 9.0 Hz, 2H), 7.39-7.29 (m, 5H), 5.51 (s, 1H), 4.97 (d, *J* = 2.6 Hz, 1H), 3.90 (d, *J* = 15.7 Hz, 1H), 3.33 (ddd, *J* = 15.2, 12.2, 2.9 Hz, 1H), 2.04-1.81 (m, 3H), 1.52-1.48 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 149.9, 146.2, 136.9, 129.1, 128.8, 128.0, 126.7, 123.9, 63.8, 51.5, 42.2, 27.2, 19.5; HRMS (EI) calcd for $C_{17}H_{17}BrN_2O_4S$ *m/z* $[M]^+$: 424.0087; found: 424.0080. HPLC (Daicel Chiralpak IC, *i*-PrOH/hexane = 45/55, 0.6 mL/min, 230 nm) t_1 = 43.9 min (major), t_2 = 48.5 min (minor).



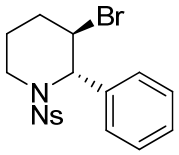
Detector A Ch1 230nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	44.347	5572945	83852	49.970	52.951
2	48.499	5579747	74507	50.030	47.049
Total		11152693	158358	100.000	100.000



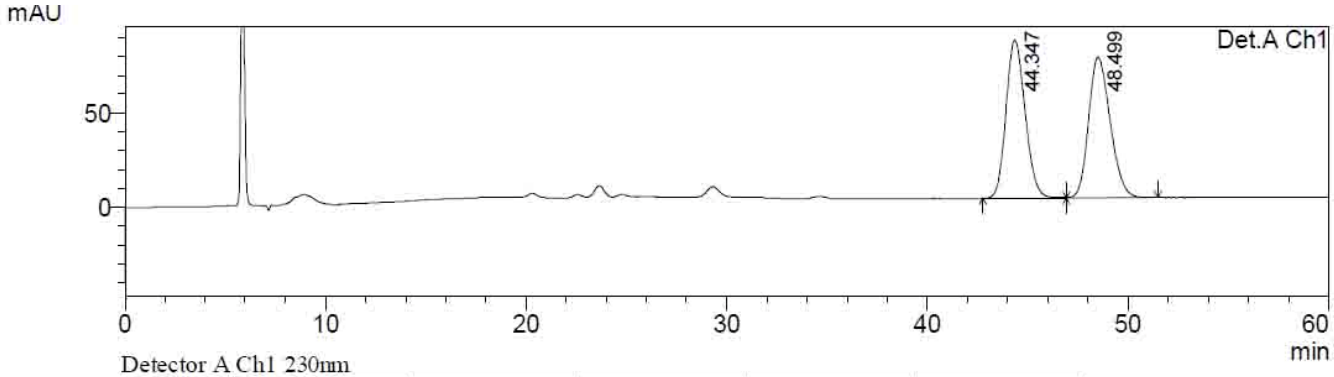
Detector A Ch1 230nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	43.894	15566957	222857	94.968	95.368
2	48.464	824771	10825	5.032	4.632
Total		16391728	233682	100.000	100.000



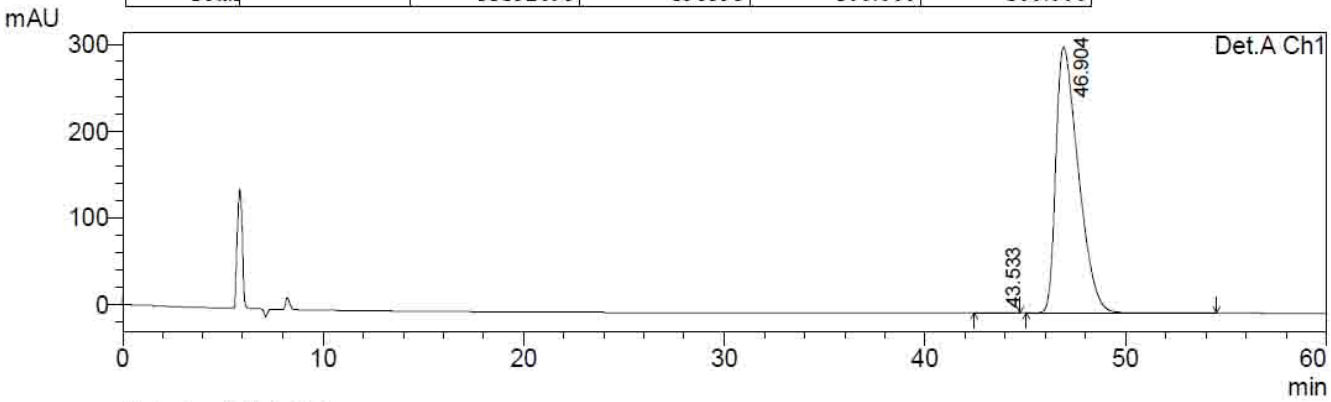
(2*R*,3*S*)-3-Bromo-1-(4-nitrophenylsulfonyl)-2-phenylpiperidine (ent-2a)

$[\alpha]_D^{26}$ +22.4 (*c* 1.0, CH_2Cl_2, 99% ee);



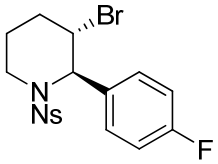
Detector A Ch1 230nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	44.347	5572945	83852	49.970	52.951
2	48.499	5579747	74507	50.030	47.049
Total		11152693	158358	100.000	100.000



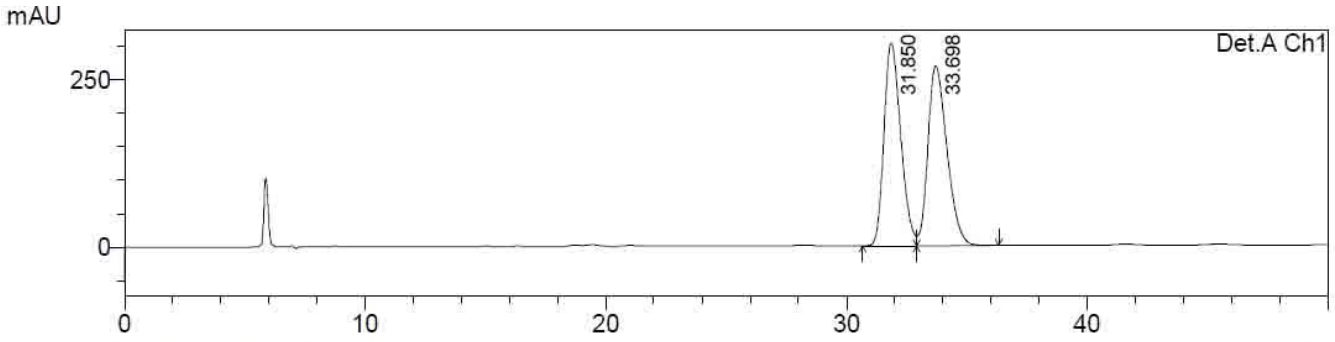
Detector A Ch1 230nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	43.533	26034	436	0.109	0.142
2	46.904	23883000	306229	99.891	99.858
Total		23909034	306665	100.000	100.000



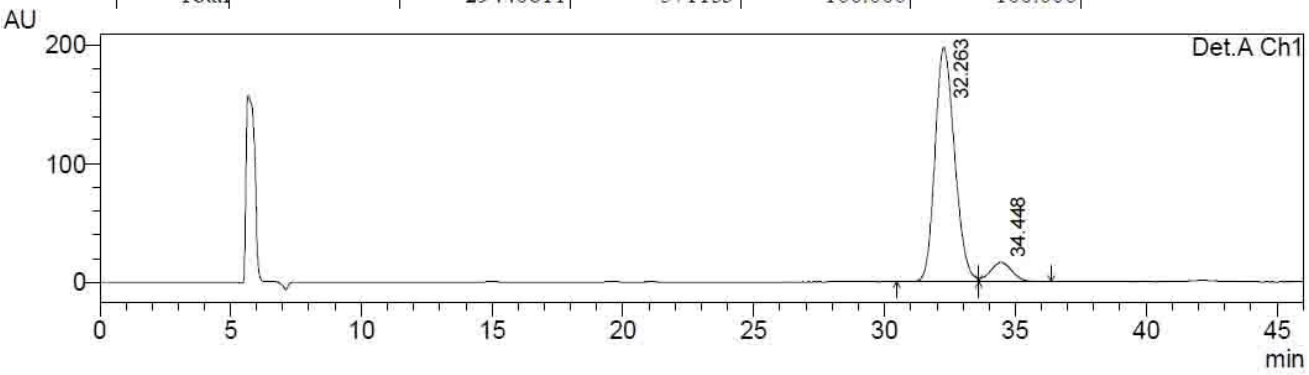
(2*S*,3*R*)-3-Bromo-2-(4-fluorophenyl)-1-(4-nitrophenylsulfonyl)piperidine (2b)

White solid, $[\alpha]_D^{26}$ –12.6 (*c* 1.0, CH_2Cl_2, 83% ee); IR (KBr): 2962, 1605, 1531, 1347, 1164, 1010 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 8.34 (d, *J* = 9.0 Hz, 2H), 8.04 (d, *J* = 9.1 Hz, 2H), 7.34-7.29 (m, 2H), 7.07 (dd, *J* = 8.5 Hz, 2H), 5.47 (s, 1H), 4.93 (dd, *J* = 5.4, 2.3 Hz, 1H), 3.86 (dd, *J* = 14.3, 2.9 Hz, 1H), 3.30 (ddd, *J* = 14.2, 12.2, 3.0 Hz, 1H), 1.95-1.83 (m, 3H), 1.54-1.48 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 162.2 (d, *J* = 247.1), 150.0, 146.0, 132.6, 128.8, 128.5 (d, *J* = 7.6 Hz), 124.0, 116.1 (d, *J* = 21.8), 63.3, 51.2, 42.1, 27.2, 19.4; HRMS (EI) calcd for $C_{17}H_{16}FBrN_2O_4S$ *m/z* $[M]^+$: 441.9993; found: 441.9992. HPLC (Daicel Chiralpak IC, *i*-PrOH/hexane = 45/55, 0.6 mL/min, 230 nm) t_1 = 32.3 min (major), t_2 = 34.4 min (minor).



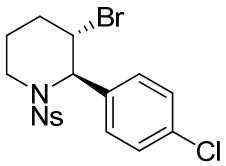
Detector A Ch1 230nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	31.850	14650455	302172	49.763	52.907
2	33.698	14790156	268962	50.237	47.093
Total		29440611	571133	100.000	100.000



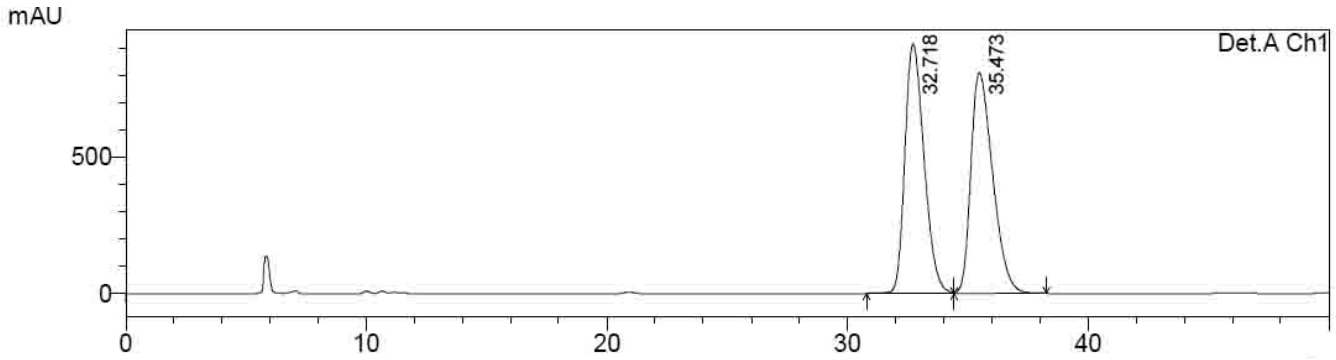
Detector A Ch1 230nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	32.263	10270267	197192	91.547	92.383
2	34.448	948361	16259	8.453	7.617
Total		11218628	213451	100.000	100.000



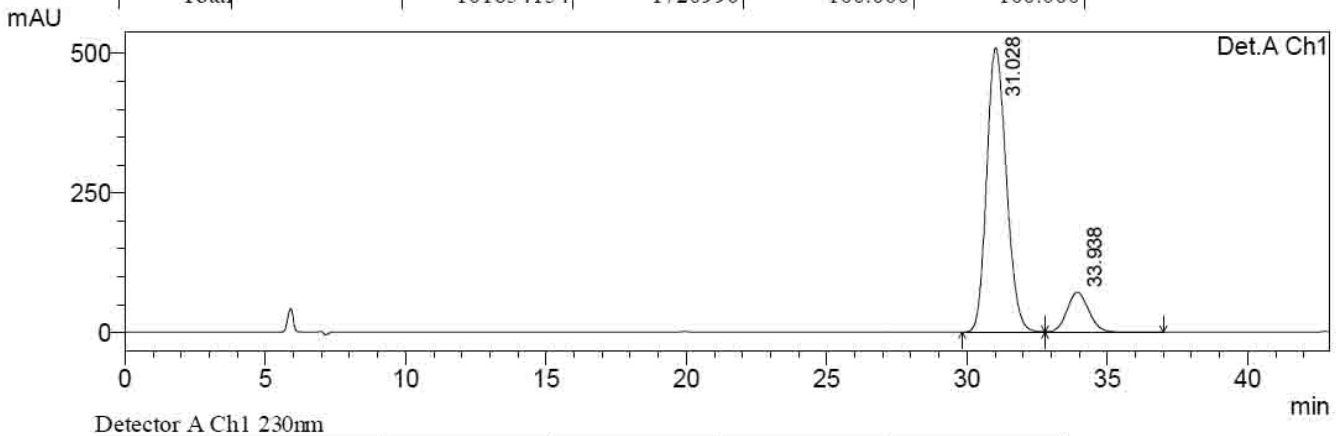
(2*S*,3*R*)-3-Bromo-2-(4-chlorophenyl)-1-(4-nitrophenylsulfonyl)piperidine (2c)

White solid, $[\alpha]_D^{26}$ –15.4 (*c* 0.57, CH_2Cl_2, 73% ee); IR (KBr): 2958, 1607, 1530, 1346, 1162, 1108 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 8.34 (d, *J* = 8.8 Hz, 2H), 8.10 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 8.2 Hz, 2H), 7.28 (d, *J* = 8.2 Hz, 2H), 5.46 (s, 1H), 4.92 (d, *J* = 3.2 Hz, 1H), 3.86 (d, *J* = 12.6 Hz, 1H), 3.29 (ddd, *J* = 14.5, 12.0, 3.2 Hz, 1H), 1.92-1.82 (m, 3H), 1.55-1.48 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.0, 146.0, 135.4, 134.1, 129.3, 128.8, 128.2, 124.0, 63.3, 51.0, 42.2, 27.3, 19.4; HRMS (EI) calcd for $C_{17}H_{16}ClBrN_2O_4S$ *m/z* $[M]^+$: 457.9697; found: 457.9693. HPLC (Daicel Chiralpak IC, *i*-PrOH/hexane = 45/55, 0.6 mL/min, 230 nm) t_1 = 31.0 min (major), t_2 = 33.9 min (minor).



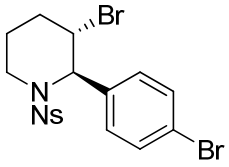
Detector A Ch1 230nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	32.718	50657898	912900	49.834	53.045
2	35.473	50996256	808090	50.166	46.955
Total		101654154	1720990	100.000	100.000



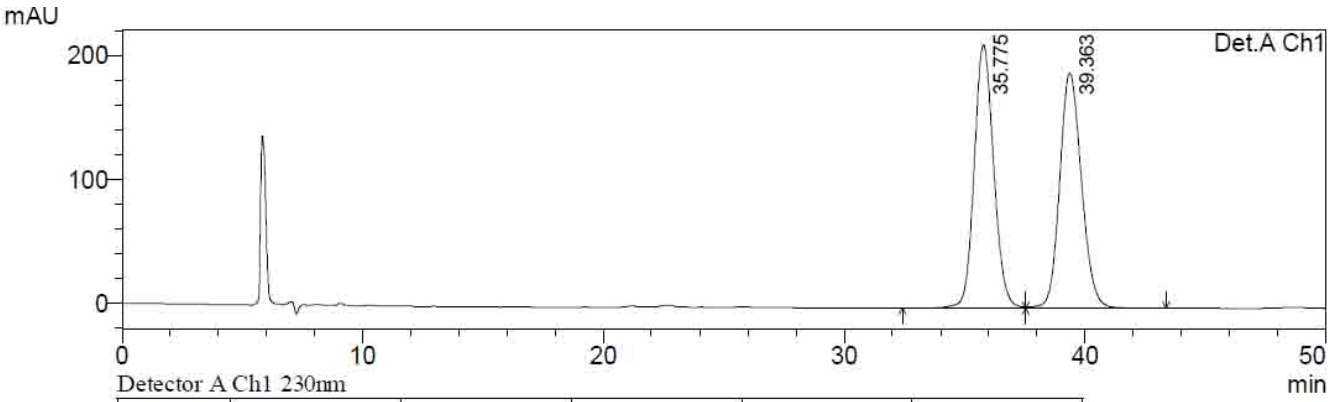
Detector A Ch1 230nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	31.028	24922230	510135	86.539	87.720
2	33.938	3876500	71417	13.461	12.280
Total		28798730	581552	100.000	100.000



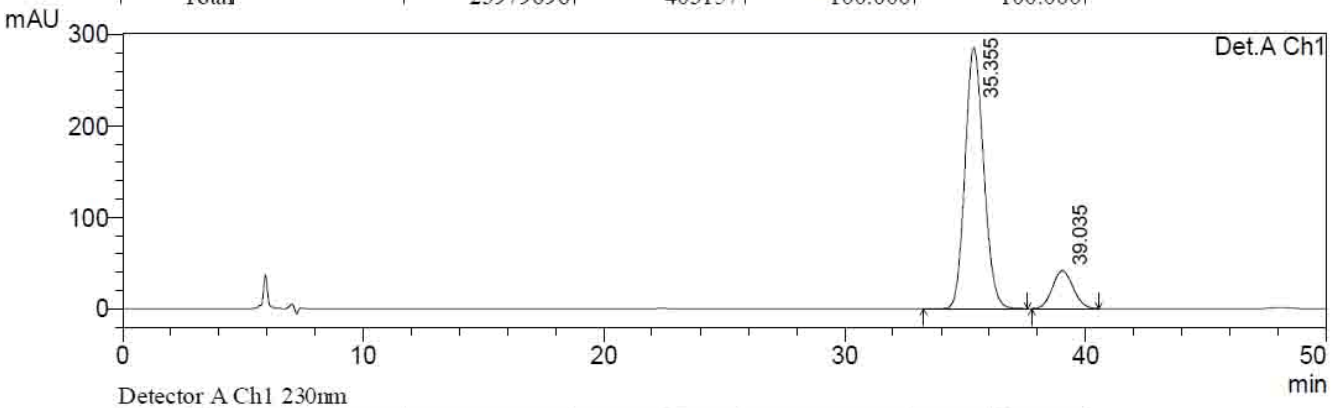
(2*S*,3*R*)-3-Bromo-2-(4-bromophenyl)-1-(4-nitrophenylsulfonyl)piperidine (2d)

White solid, $[\alpha]_D^{25}$ –17.4 (*c* 1.0, CH_2Cl_2, 72% ee); IR (KBr): 2927, 1523, 1489, 1350, 1160, 1109 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 8.34 (d, *J* = 8.7 Hz, 2H), 8.10 (d, *J* = 8.7 Hz, 2H), 7.51 (d, *J* = 8.5 Hz, 2H), 7.22 (d, *J* = 8.5 Hz, 2H), 5.43 (s, 1H), 4.92 (d, *J* = 2.5 Hz, 1H), 3.86 (d, *J* = 13.3 Hz, 1H), 3.29 (ddd, *J* = 14.9, 12.2, 2.8 Hz, 1H), 1.93-1.79 (m, 3H), 1.51-1.25 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.1, 146.0, 136.0, 132.3, 128.9, 128.5, 124.0, 122.2, 63.4, 50.9, 42.2, 27.4, 19.5; HRMS (EI) calcd for $C_{17}H_{16}Br_2N_2O_4S$ *m/z* $[M]^+$: 501.9192; found: 501.9200. HPLC (Daicel Chiralpak IC, *i*-PrOH/hexane = 40/60, 0.6 mL/min, 230 nm) t_1 = 35.4 min (major), t_2 = 39.0 min (minor).



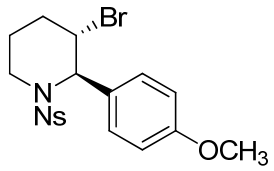
Detector A Ch1 230nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	35.775	11997862	212991	50.033	52.831
2	39.363	11981834	190166	49.967	47.169
Total		23979696	403157	100.000	100.000



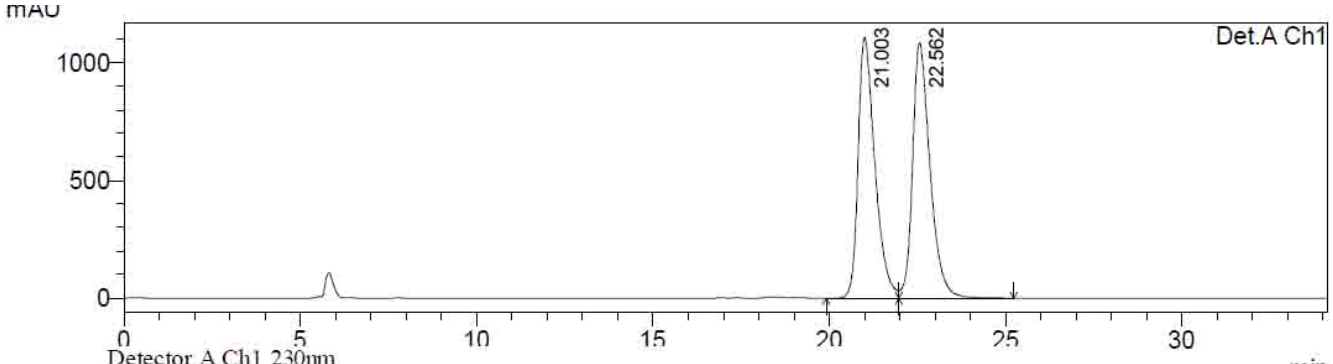
Detector A Ch1 230nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	35.355	15419007	285099	86.136	87.336
2	39.035	2481799	41340	13.864	12.664
Total		17900806	326439	100.000	100.000



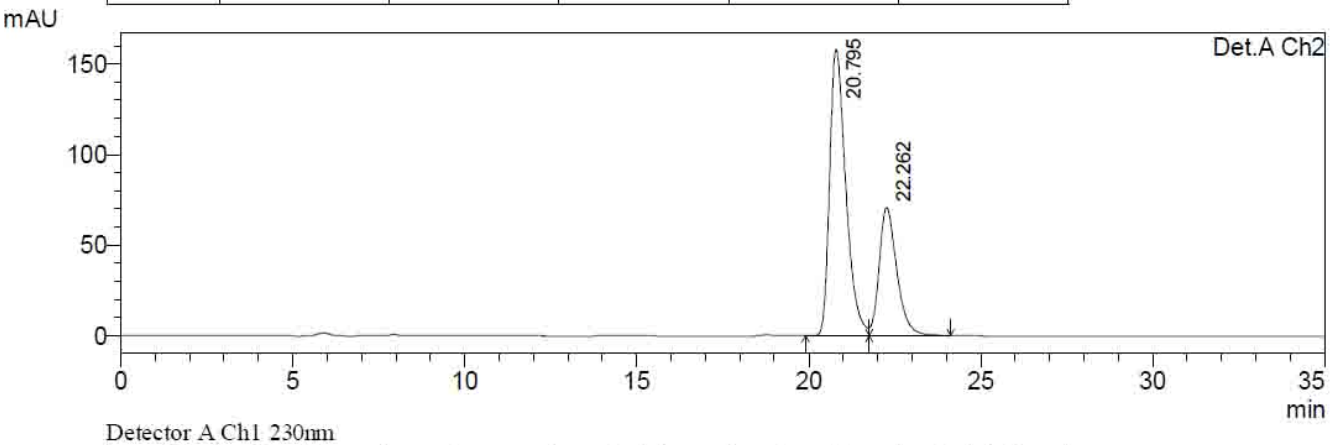
(2*S*,3*R*)-3-Bromo-2-(4-methoxyphenyl)-1-(4-nitrophenylsulfonyl)piperidine (2e)

White solid, $[\alpha]_D^{25}$ –4.0 (*c* 0.5, CH_2Cl_2, 34% ee); IR (KBr): 2954, 1607, 1525, 1351, 1162, 1107 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 8.32 (d, *J* = 8.8 Hz, 2H), 8.04 (d, *J* = 8.9 Hz, 2H), 7.34 (d, *J* = 1.9 Hz, 1H), 7.26 (s, 1H), 6.87 (d, *J* = 8.8 Hz, 1H), 5.40 (s, 1H), 4.85 (dd, *J* = 5.6, 2.9 Hz, 1H), 3.89 (s, 3H), 3.89-3.86 (m, 1H), 3.30 (ddd, *J* = 14.4, 11.4, 2.6 Hz, 1H), 1.97-1.87 (m, 4H), 1.55-1.42 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.5, 150.0, 146.0, 131.6, 130.2, 128.7, 127.3, 124.0, 112.2, 112.1, 62.9, 56.3, 51.0, 42.3, 27.3, 19.6; HRMS (EI) calcd for $C_{18}H_{19}BrN_2O_5S$ *m/z* $[M]^+$: 454.0193; found: 454.0190. HPLC (Daicel Chiralpak IB, *i*-PrOH/hexane = 45/55, 0.6 mL/min, 230 nm) t_1 = 20.8 min (major), t_2 = 22.3 min (minor).



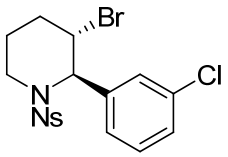
Detector A Ch1 230nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.003	36729598	1108802	49.522	50.552
2	22.562	37438867	1084574	50.478	49.448
Total		74168465	2193376	100.000	100.000



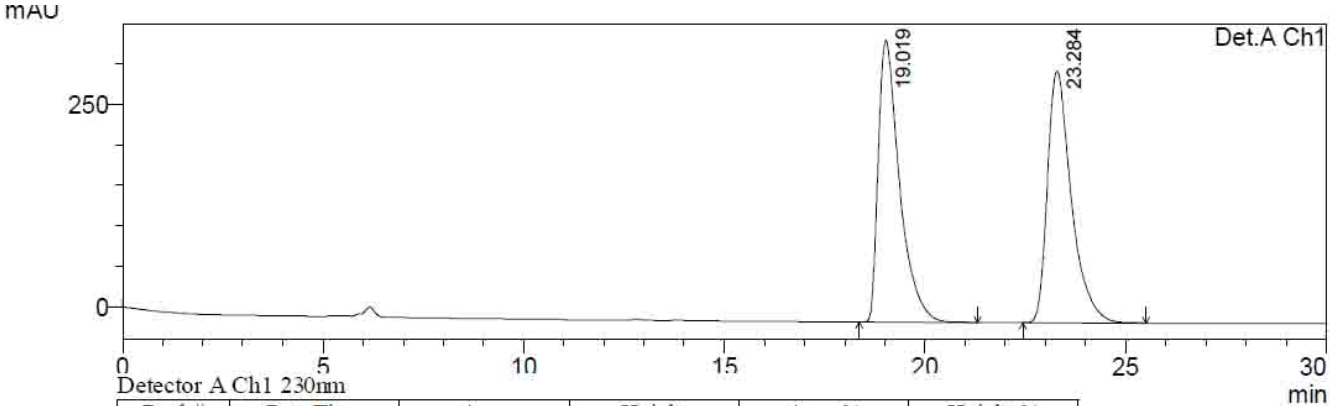
Detector A Ch1 230nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.793	13298165	405460	67.044	69.066
2	22.260	6536819	181599	32.956	30.934
Total		19834984	587059	100.000	100.000



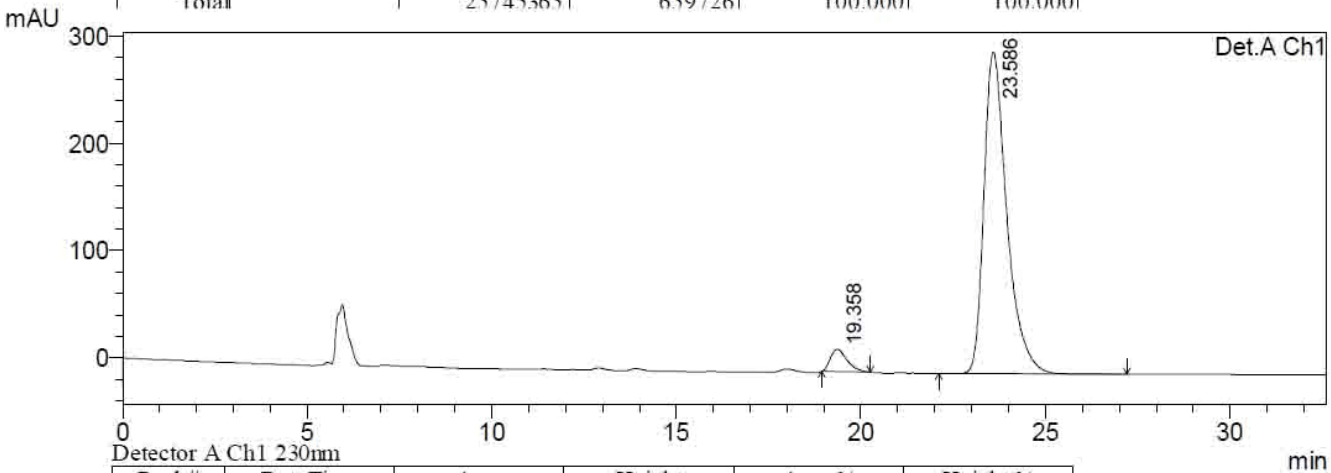
(2*S*,3*R*)-3-Bromo-2-(3-chlorophenyl)-1-(4-nitrophenylsulfonyl)piperidine (2f)

White solid, $[\alpha]_D^{25}$ –24.2 (*c* 1.0, CH_2Cl_2, 90% ee); IR (KBr): 2928, 1526, 1346, 1160, 1108, 951 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.33 (d, *J* = 8.9 Hz, 2H), 8.07 (d, *J* = 8.9 Hz, 2H), 7.34-7.28 (m, 2H), 7.26-7.21 (m, 2H), 5.46 (s, 1H), 4.90 (dd, *J* = 5.6, 2.8 Hz, 1H), 3.90 (dd, *J* = 13.8, 2.8 Hz, 1H), 3.31 (ddd, *J* = 13.9, 12.0, 2.9 Hz, 1H), 2.04-1.82 (m, 3H), 1.55-1.50 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.0, 145.9, 139.0, 135.2, 130.5, 128.8, 128.3, 127, 125.0, 124.1, 63.3, 50.8, 42.3, 27.3, 19.4; HRMS (EI) calcd for $C_{17}H_{16}ClBrN_2O_4S$ *m/z* $[M]^+$: 457.9697; found: 457.9693. HPLC (Daicel Chiralpak AD, *i*-PrOH/hexane = 40/60, 0.6 mL/min, 230 nm) t_1 = 19.4 min (minor), t_2 = 23.6 min (major).



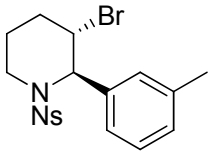
Detector A Ch1 230nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.019	12854526	348665	49.929	52.850
2	23.284	12890840	311061	50.071	47.150
Total		25745365	659726	100.000	100.000



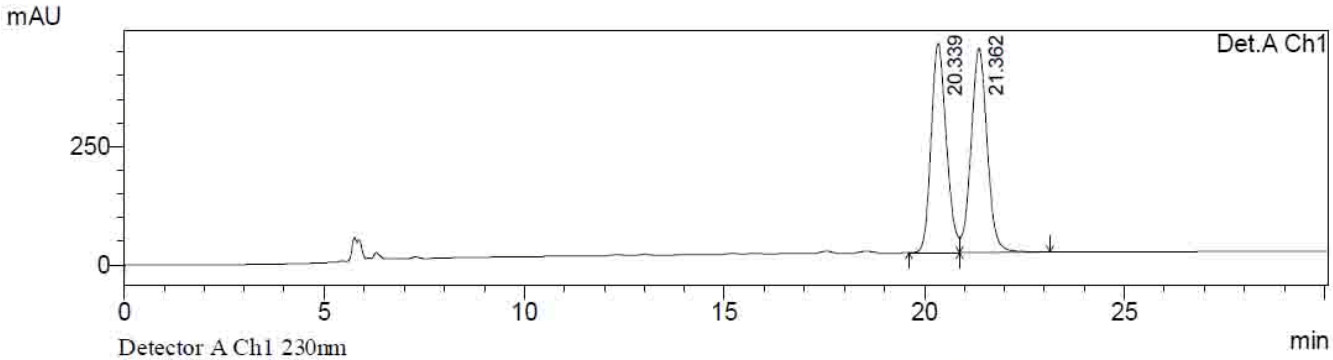
Detector A Ch1 230nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.358	664493	20985	4.891	6.535
2	23.586	12920267	300118	95.109	93.465
Total		13584761	321103	100.000	100.000



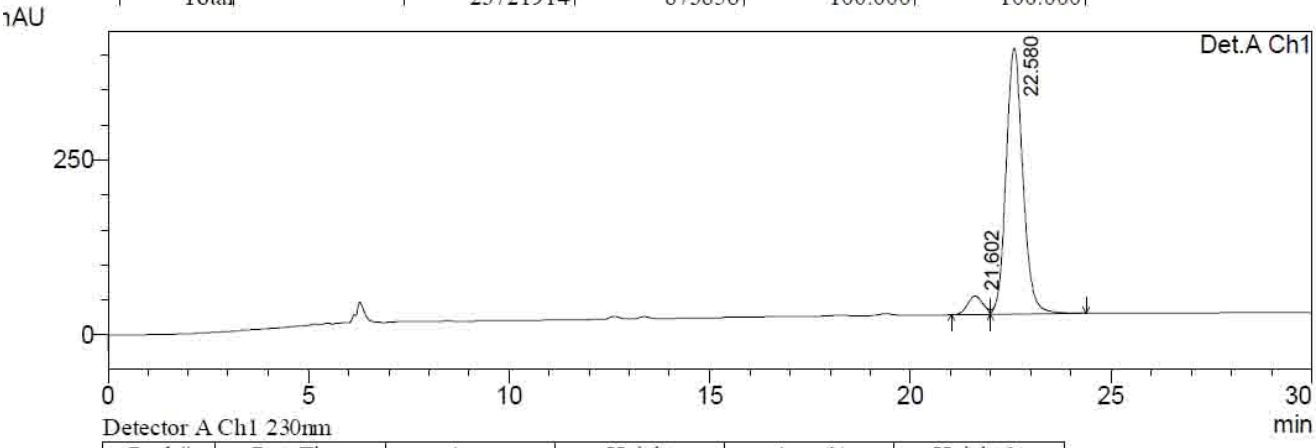
(2*S*,3*R*)-3-Bromo-1-(4-nitrophenylsulfonyl)-2-*p*-tolylpiperidine (2g)

White solid, $[\alpha]_D^{25}$ –17.5 (*c* 1.0, CH_2Cl_2, 88% ee); IR (KBr): 2927, 1526, 1346, 1160, 1108 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 8.30 (d, *J* = 8.8 Hz, 2H), 8.05 (d, *J* = 8.8 Hz, 2H), 7.23 (dd, *J* = 7.7 Hz, 1H), 7.09 (d, *J* = 8.5 Hz, 2H), 7.04 (s, 1H), 5.47 (s, 1H), 4.95 (dd, *J* = 5.6, 2.9 Hz, 1H), 3.90 (dd, *J* = 14.0, 2.9 Hz, 1H), 3.35 (ddd, *J* = 14.8, 12.0, 3.1 Hz, 1H), 2.32 (s, 3H), 1.98-1.83 (m, 3H), 1.53-1.49 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 149.8, 146.2, 138.9, 136.8, 129.0, 128.8, 128.7, 127.4, 123.9, 123.8, 63.8, 51.7, 42.3, 27.2, 21.6, 19.5; HRMS (EI) calcd for $C_{18}H_{19}BrN_2O_4S$ *m/z* $[M]^+$: 438.0243; found: 438.0233. HPLC (Daicel Chiralpak IA, *i*-PrOH/hexane = 15/85, 0.6 mL/min, 230 nm) t_1 = 21.6 min (minor), t_2 = 22.6 min (major).



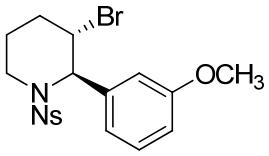
Detector A Ch1 230nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.339	11682866	442374	49.249	50.623
2	21.362	12039048	431482	50.751	49.377
Total		23721914	873856	100.000	100.000



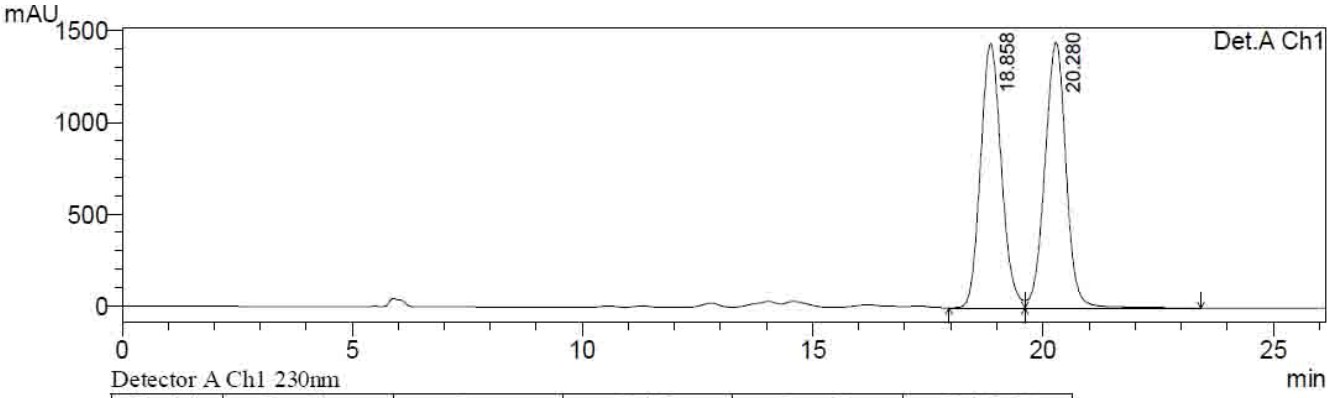
Detector A Ch1 230nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.602	712851	26574	6.056	6.544
2	22.580	11057505	379483	93.944	93.456
Total		11770356	406057	100.000	100.000



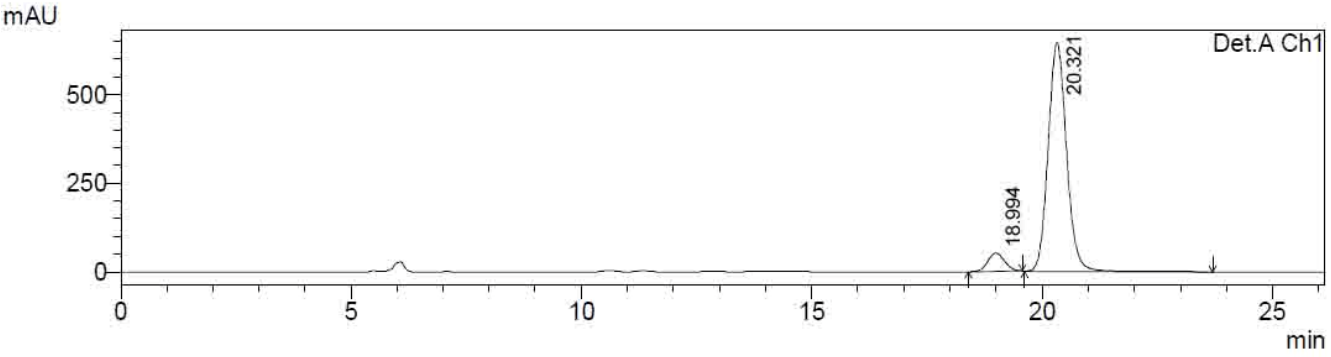
(2*S*,3*R*)-3-Bromo-2-(3-methoxyphenyl)-1-(4-nitrophenylsulfonyl)piperidine (2h)

White solid, $[\alpha]_D^{25}$ –11.8 (*c* 1.0, CH_2Cl_2, 86% ee); IR (KBr): 3021, 1531, 1349, 1216, 1164 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.30 (d, *J* = 9.0 Hz, 2H), 8.02 (d, *J* = 9.0 Hz, 2H), 7.29-7.25 (m, 1H), 6.88-6.80 (m, 3H), 5.48 (s, 1H), 4.95 (dd, *J* = 5.5, 2.9 Hz, 1H), 3.88 (dd, *J* = 13.8, 2.8 Hz, 1H), 3.78 (s, 3H), 3.33 (ddd, *J* = 13.9, 12.0, 2.9 Hz, 1H), 1.99-1.86 (m, 3H), 1.53-1.49 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.2, 149.9, 146.1, 138.5, 130.2, 128.8, 123.9, 118.9, 113.2, 112.8, 63.7, 55.3, 51.5, 42.3, 27.2, 19.4; HRMS (EI) calcd for $C_{18}H_{19}BrN_2O_5S$ *m/z* $[M]^+$: 454.0193; found: 454.0190. HPLC (Daicel Chiralpak IA, *i*-PrOH/hexane = 40/60, 0.6 mL/min, 230 nm) t_1 = 19.0 min (minor), t_2 = 20.3 min (major).



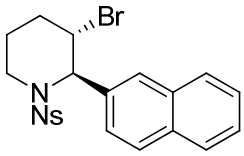
Detector A Ch1 230nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.858	45225328	1439763	49.486	49.880
2	20.280	46164085	1446693	50.514	50.120
Total		91389413	2886457	100.000	100.000



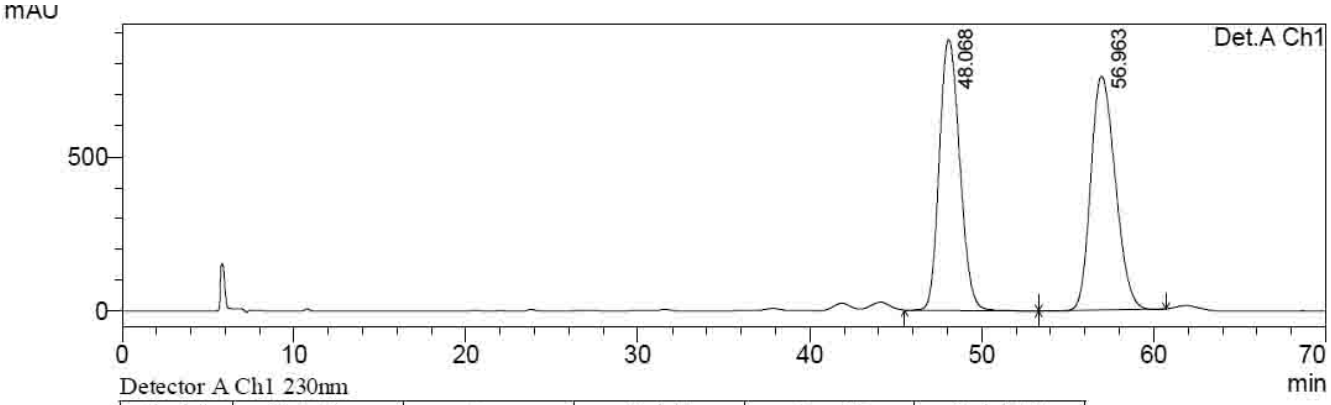
Detector A Ch1 230nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.994	1313686	51725	6.868	7.430
2	20.321	17813709	644418	93.132	92.570
Total		19127395	696143	100.000	100.000



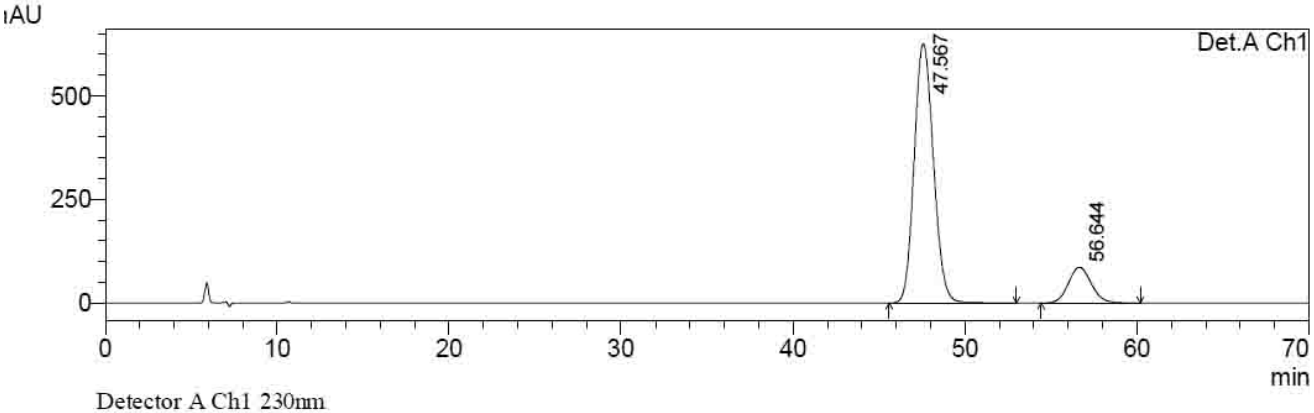
(2*S*,3*R*)-3-Bromo-2-(naphthalen-2-yl)-1-(4-nitrophenylsulfonyl)piperidine (2i)

White solid, $[\alpha]_D^{25}$ –19.6 (*c* 1.0, CH_2Cl_2, 72% ee); IR (KBr): 2943, 1532, 1351, 1310, 1161, 1107 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.25 (d, *J* = 8.8 Hz, 2H), 8.06 (d, *J* = 8.8 Hz, 2H), 7.85-7.82 (m, 2H), 7.73 (d, *J* = 5.8 Hz, 1H), 7.67 (s, 1H), 7.53-7.48 (m, 2H), 7.41 (dd, *J* = 8.6, 1.8 Hz, 1H), 5.64 (s, 1H), 5.90 (dd, *J* = 5.8, 2.8 Hz, 1H), 3.96 (d, *J* = 13.7 Hz, 1H), 3.47 (ddd, *J* = 13.8, 11.0, 3.0 Hz, 1H), 2.04-1.91 (m, 3H), 1.57-1.53 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.9, 146.2, 134.2, 133.1, 132.6, 129.1, 128.8, 128.0, 127.6, 126.78, 126.76, 126.2, 124.3, 123.9 64.1, 51.4, 52.6, 27.5, 19.7; HRMS (EI) calcd for $C_{21}H_{19}BrN_2O_4S$ *m/z* $[M]^+$: 474.0243; found: 474.0233. HPLC (Daicel Chiralpak IC, *i*-PrOH/hexane = 40/60, 0.6 mL/min, 230 nm) t_1 = 47.6 min (major), t_2 = 56.6 min (minor).



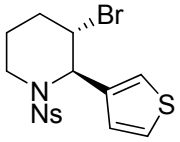
Detector A Ch1 230nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	48.068	72469901	878289	49.174	53.707
2	56.963	74903061	757040	50.826	46.293
Total		147372962	1635329	100.000	100.000



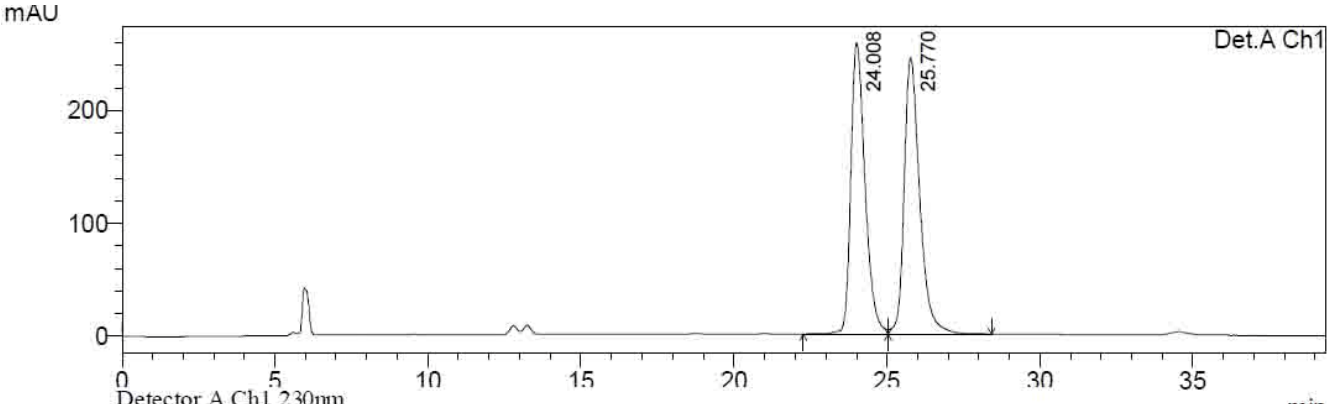
Detector A Ch1 230nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	47.567	48674211	624806	86.004	87.912
2	56.644	7921048	85909	13.996	12.088
Total		56595259	710715	100.000	100.000



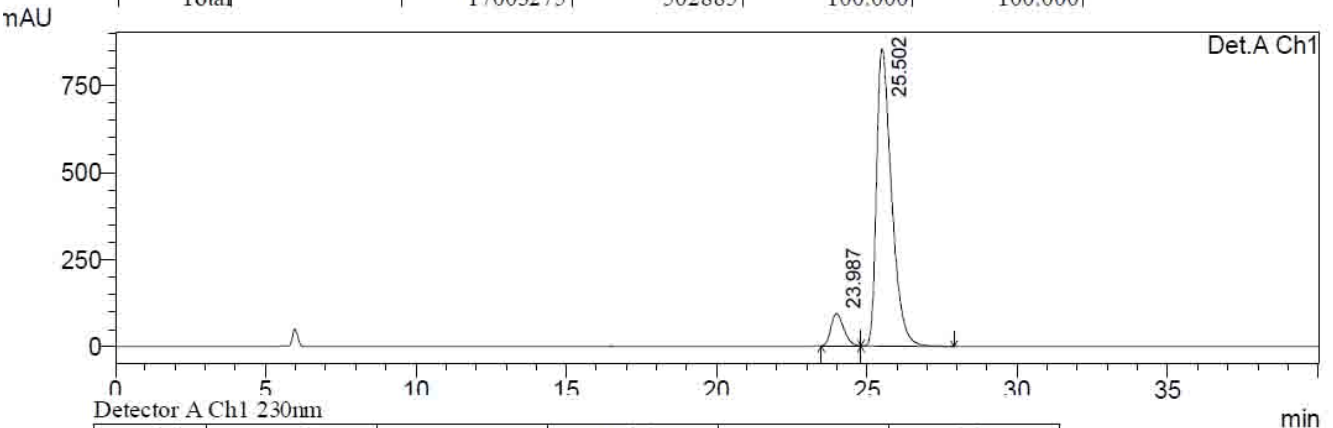
(2*S*,3*R*)-3-Bromo-1-(4-nitrophenylsulfonyl)-2-(thiophen-3-yl)piperidine (2j)

White solid, $[\alpha]_D^{25}$ –17.8 (*c* 0.5, CH_2Cl_2, 83% ee); IR (KBr): 2960, 1525, 1344, 1168, 1093 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.32 (d, *J* = 8.8 Hz, 2H), 8.08 (d, *J* = 8.9 Hz, 2H), 7.34 (dd, *J* = 5.0, 2.9 Hz, 1H), 7.17-7.16 (m, 1H), 7.02 (d, *J* = 5.0 Hz, 1H), 5.51 (s, 1H), 4.87 (brs, 1H), 3.78 (d, *J* = 13.0 Hz, 1H), 3.24 (ddd, *J* = 13.9, 12.0, 2.7 Hz, 1H), 1.99-1.88 (m, 3H), 1.54-1.48 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.9, 146.0, 138.1, 128.8, 127.1, 126.4, 124.0, 123.0, 61.0, 50.8, 41.7, 27.4, 19.5; HRMS (EI) calcd for $C_{15}H_{15}BrN_2O_4S_2$ *m/z* $[M]^+$: 429.9651; found: 429.9654. HPLC (Daicel Chiralpak IB, *i*-PrOH/hexane = 30/70, 0.6 mL/min, 230 nm) t_1 = 24.0 min (minor), t_2 = 25.5 min (major).



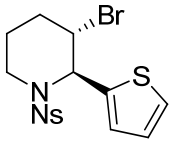
Detector A Ch1 230nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.008	8340891	257988	49.055	51.302
2	25.770	8662384	244897	50.945	48.698
Total		17003275	502885	100.000	100.000



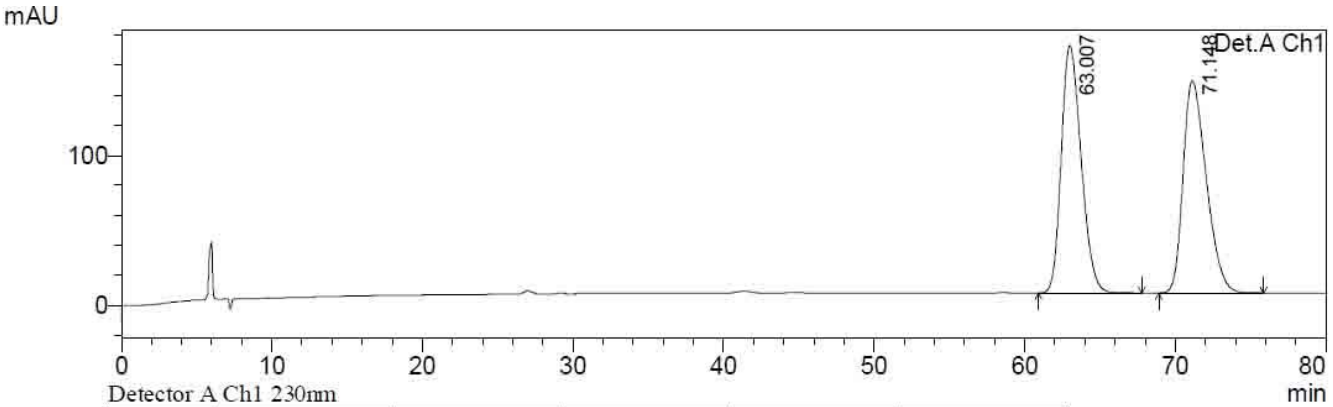
Detector A Ch1 230nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	23.987	2763745	93131	8.501	9.839
2	25.502	29747587	853370	91.499	90.161
Total		32511332	946501	100.000	100.000



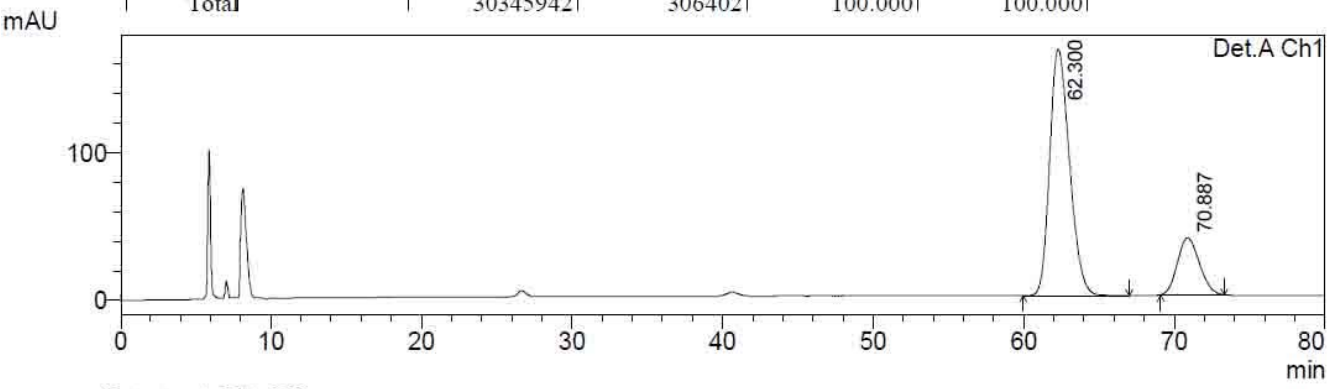
(2*S*,3*R*)-3-Bromo-1-(4-nitrophenylsulfonyl)-2-(thiophen-2-yl)piperidine (2k)

White solid, $[\alpha]_D^{25}$ –20.2 (*c* 1.0, CH_2Cl_2, 59% ee); IR (KBr): 2944, 1532, 1350, 1162, 1092 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 8.26 (d, *J* = 8.9 Hz, 2H), 7.97 (d, *J* = 8.7 Hz, 2H), 7.23 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.02 (dd, *J* = 2.5, 1.2 Hz, 1H), 6.98 (dd, *J* = 5.1, 3.7 Hz, 1H), 5.73 (s, 1H), 4.72 (d, *J* = 2.3 Hz, 1H), 3.83 (dd, *J* = 13.3, 3.7 Hz, 1H), 3.24 (ddd, *J* = 13.3, 10.3, 3.0 Hz, 1H), 2.19-2.00 (m, 3H), 1.98-1.58 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 149.9, 145.7, 139.6, 128.7, 127.1, 127.0, 125.9, 123.9, 60.5, 50.8, 41.6, 27.2, 19.4; HRMS (EI) calcd for $C_{15}H_{15}BrN_2O_4S_2$ *m/z* $[M]^+$: 429.9651; found: 429.9666. HPLC (Daicel Chiralpak IC, *i*-PrOH/hexane = 40/60, 0.6 mL/min, 230 nm) t_1 = 62.3 min (major), t_2 = 70.9 min (minor).



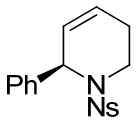
Detector A Ch1 230nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	63.007	15182248	165078	50.031	53.876
2	71.148	15163694	141324	49.969	46.124
Total		30345942	306402	100.000	100.000



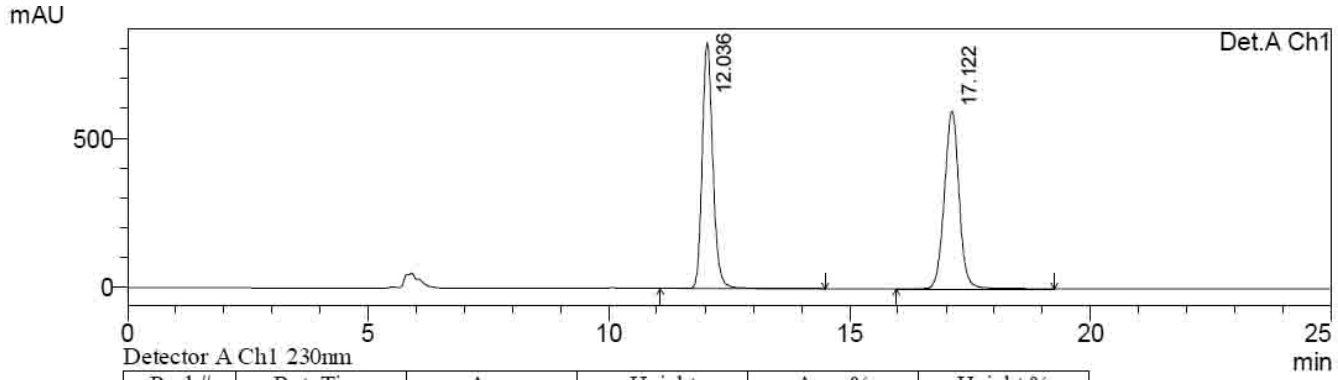
Detector A Ch1 230nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	62.300	15305051	166886	79.621	81.232
2	70.887	3917432	38557	20.379	18.768
Total		19222483	205443	100.000	100.000



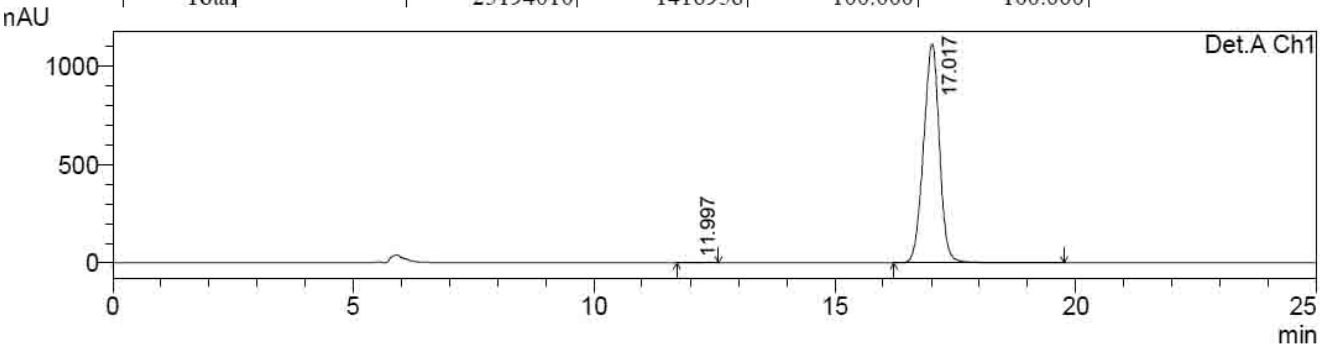
(*R*)-1-(4-Nitrophenylsulfonyl)-6-phenyl-1,2,3,6-tetrahydropyridine (7)

White solid, $[\alpha]_D^{25}$ +264.6 (*c* 1.0, CH_2Cl_2, 99% ee); IR (KBr): 2932, 1532, 1346, 1163, 1097, 940 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.21 (d, *J* = 8.9 Hz, 2H), 7.85 (d, *J* = 8.9 Hz, 2H), 7.37-7.35 (m, 2H), 7.31-7.28 (m, 3H), 5.93-5.89 (m, 1H), 5.85-5.80 (m, 1H), 5.53 (s, 1H), 3.85 (ddd, *J* = 13.8, 6.2, 1.0 Hz, 1H), 3.15 (ddd, *J* = 16.2, 11.3, 5.0 Hz, 1H), 2.14-1.97 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.7, 146.9, 138.7, 128.5, 128.3 (2 carbons), 128.2, 128.1, 126.0, 124.0, 56.6, 38.7, 23.8; HRMS (EI) calcd for $C_{17}H_{16}N_2O_4S$ *m/z* $[M]^+$: 344.0825; found: 344.0834. HPLC (Daicel Chiralpak IA, *i*-PrOH/hexane = 40/60, 0.6 mL/min, 230 nm) t_1 = 12.0 min (minor), t_2 = 17.0 min (major).



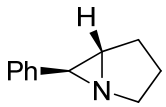
Detector A Ch1 230nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.036	12594530	823013	49.990	58.083
2	17.122	12599480	593945	50.010	41.917
Total		25194010	1416958	100.000	100.000



Detector A Ch1 230nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.997	25780	1585	0.101	0.142
2	17.017	25616311	1114120	99.899	99.858
Total		25642091	1115706	100.000	100.000

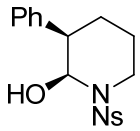


(6*S*)-6-Phenyl-1-azabicyclo[3.1.0]hexane (8)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29-7.18 (m, 5H), 3.20 (ddd, *J* = 12.2, 8.4, 1.3 Hz, 1H), 3.05 (dt, *J* = 11.5, 7.6 Hz, 1H), 2.44 (d, *J* = 4.8, 2.8 Hz, 1H), 2.35 (d, *J* = 2.6 Hz, 1H), 2.23 (d, *J* = 13.3, 8.1 Hz, 1H), 2.03-1.93 (m, 1H), 1.78-1.70 (m, 1H), 1.65-1.56 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.2, 128.2, 126.7, 126.0, 53.1, 50.6, 39.7, 26.6, 20.7; HRMS (ESI) calcd for $C_{11}H_{14}N$ *m/z* $[M + H]^+$: 160.1121; found: 160.1114.

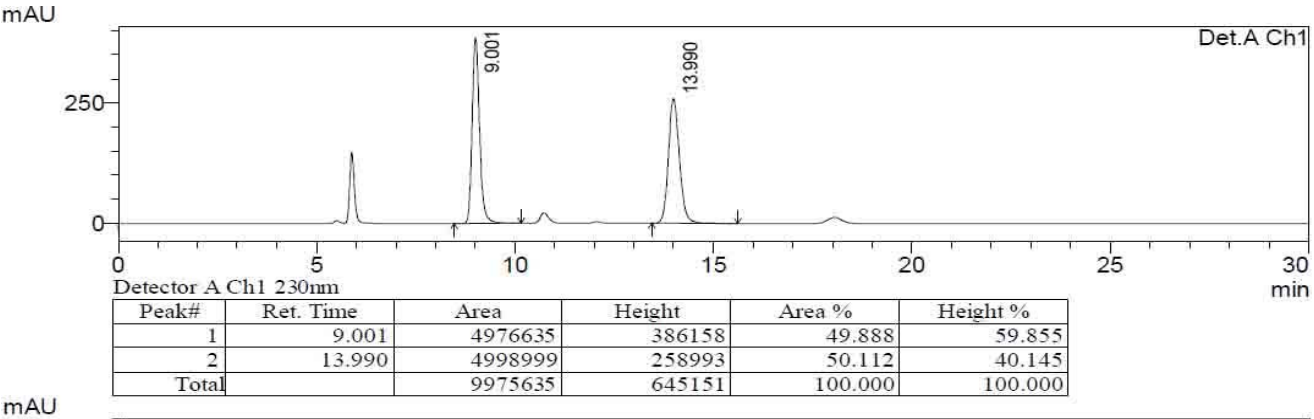
(E) Representative procedure for the silver salt mediated rearrangement

A solution of **ent-2a** (85 mg, 0.2 mmol, 1.0 eq) and silver trifluoroacetate (133 mg, 0.6 mmol, 3.0 eq) in acetone (3.0 mL) and water (1.0 mL) was stirred at 60 °C for 8 h in dark. After the mixture was cooled to room temperature, to the solution was added sat. NaCl (2.0 mL) and stirred for 5 min. The mixture was filtered by celite and washed with EtOAc. The filtrate was separated and the aqueous phase was extracted with EtOAc (3 × 5 mL). The combined extracts were washed with brine, dried and concentrated in *vacuo*. The residue was purified by column chromatography to give the desired product **ent-3a** as a yellow solid (50 mg, 68%).



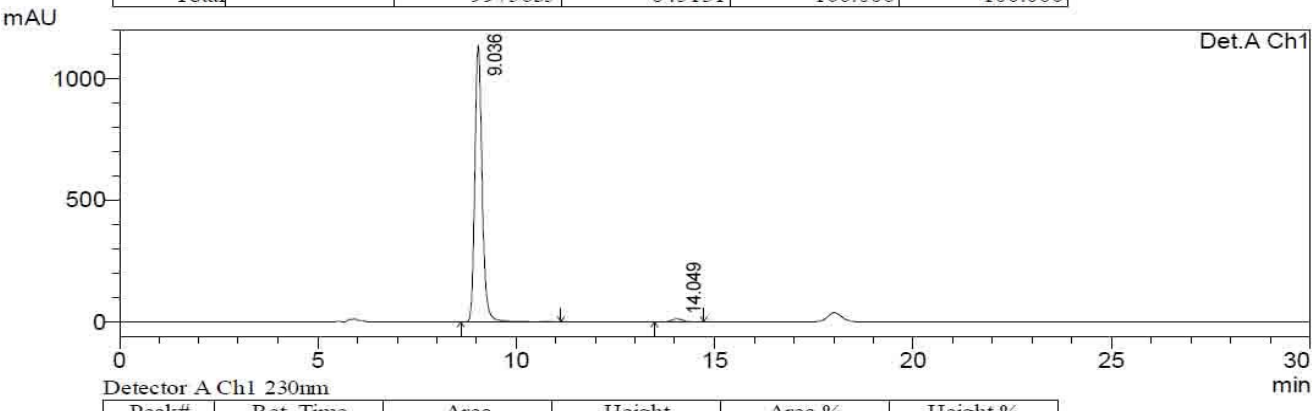
(2*S*,3*S*)-1-(4-nitrophenylsulfonyl)-2-phenylpiperidin-3-ol (ent-3a)

$[\alpha]_D^{25}$ −110.9 (*c* 1.0, CH_2Cl_2, 99% ee); IR (KBr): 3491, 2946, 1527, 1348, 1165, 1089 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.31 (d, *J* = 8.9 Hz, 2H), 8.04 (d, *J* = 8.9 Hz, 2H), 7.37-7.34 (m, 2H), 7.28-7.25 (m, 3H), 5.64 (t, *J* = 2.9 Hz, 1H), 3.69 (dt, *J* = 12.7, 2.9 Hz, 1H), 3.05-2.97 (m, 2H), 2.16-2.05 (m, 1H), 1.98-1.93 (m, 1H), 1.86-1.75 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.0, 145.3, 140.2, 129.1, 128.9, 128.0, 127.6, 124.0, 79.9, 47.5, 40.2, 25.1, 21.8; HRMS (ESI) calcd for $C_{17}H_{17}N_2O_5S$ *m/z* $[M - H]^-$: 361.0864; found: 361.0864. HPLC (Daicel Chiralpak IA, *i*-PrOH/hexane = 40/60, 0.6 mL/min, 230 nm) t_1 = 9.0 min (major), t_2 = 14.0 min (minor).



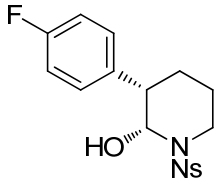
Detector A Ch1 230nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.001	4976635	386158	49.888	59.855
2	13.990	4998999	258993	50.112	40.145
Total		9975635	645151	100.000	100.000



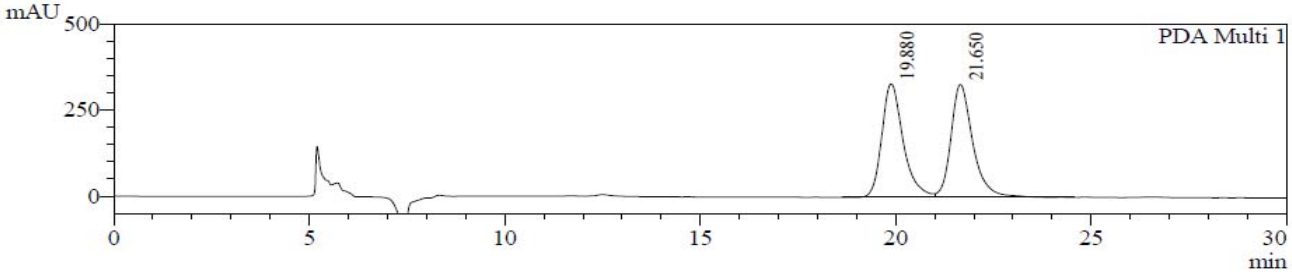
Detector A Ch1 230nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.036	14618089	1136950	98.373	98.901
2	14.049	241791	12638	1.627	1.099
Total		14859881	1149588	100.000	100.000



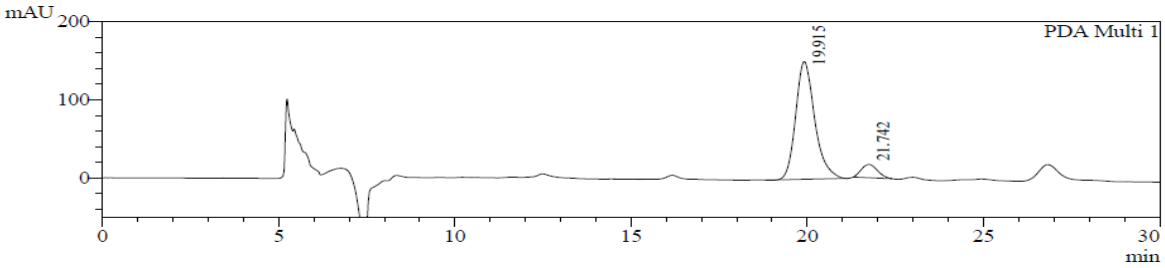
(2*R*,3*R*)-3-(4-fluorophenyl)-1-(4-nitrophenylsulfonyl)piperidin-2-ol (3b)

Yellow oil. $[\alpha]_D^{25}$ +18 (*c* 1.0, $CHCl_3$, 83% ee); IR (film): 3498, 2929, 1530, 1349, 1164, 1091 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 8.33 (d, *J* = 8.8 Hz, 2H), 8.05 (d, *J* = 8.8 Hz, 2H), 7.25 – 7.21 (m, 2H), 7.05 (d, *J* = 8.6 Hz, 2H), 5.61 (s, 1H), 3.70 (d, *J* = 11.3 Hz, 1H), 3.04 – 2.98 (m, 2H), 2.07 (dd, *J* = 13.0, 3.6 Hz, 1H), 1.95 (d, *J* = 13.6 Hz, 1H), 1.81 – 1.73 (m, 3H) ; ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.1 (d, *J* = 245.1 Hz), 150.1, 145.3, 136.0 (d, *J* = 3.1 Hz), 129.6 (d, *J* = 8.0 Hz), 129.0, 124.1, 115.7 (d, *J* = 21.1 Hz), 79.7, 46.8, 40.1, 29.7, 25.1, 22.2; HRMS (ESI) calcd for $C_{17}H_{17}FN_2O_5SNa$ *m/z* $[M + Na]^+$: 403.0734; found: 403.0740. HPLC (Daicel Chiralpak IC, *i*-PrOH/hexane = 15/85, 0.6 mL/min, 230 nm) t_1 = 19.9 min (major), t_2 = 21.7 min (minor).



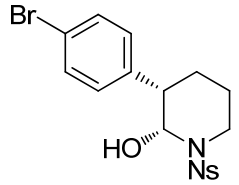
PDA Ch1 230nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.880	12584568	329695	49.660	50.152
2	21.650	12757075	327699	50.340	49.848
Total		25341643	657393	100.000	100.000



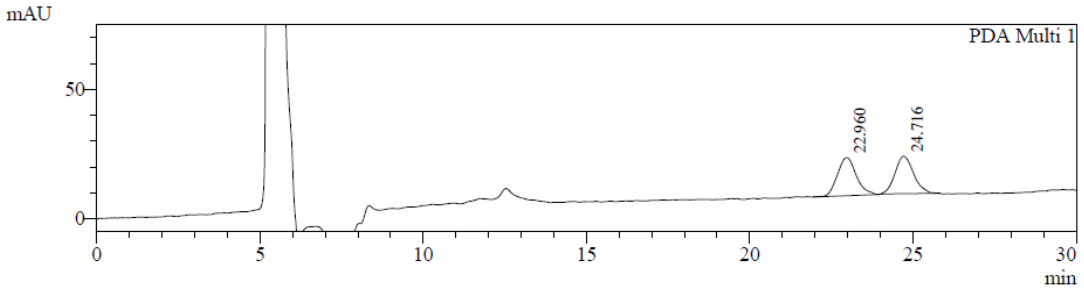
PDA Ch1 230nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.915	5674005	150756	91.292	89.801
2	21.742	541226	17122	8.708	10.199
Total		6215231	167878	100.000	100.000



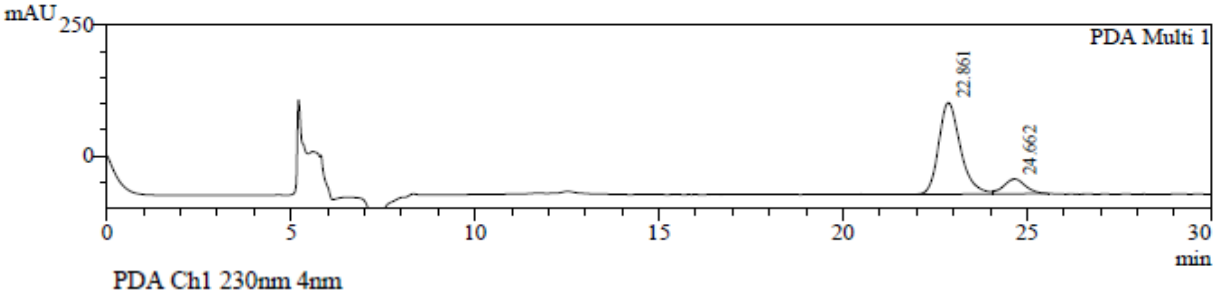
(2*R*,3*R*)-3-(4-bromophenyl)-1-(4-nitrophenylsulfonyl)piperidin-2-ol (3d)

Yellow oil. $[\alpha]_D^{25}$ +27 (*c* 1.0, $CHCl_3$, 72% ee); IR (film): 3369, 2923, 1532, 1349, 1162, 1009 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 8.33 (d, *J* = 8.8 Hz, 2H), 8.04 (d, *J* = 8.8 Hz, 2H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.14 (d, *J* = 8.4 Hz, 2H), 5.63 – 5.59 (m, 1H), 3.69 (d, *J* = 11.8 Hz, 1H), 3.02 (dd, *J* = 16.9, 7.5 Hz, 1H), 2.98 – 2.93 (m, 1H), 2.05 (dd, *J* = 12.0, 4.6 Hz, 1H), 1.95 (d, *J* = 13.7 Hz, 1H), 1.82 – 1.73 (m, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.1, 145.3, 139.3, 132.0, 129.8, 129.0, 124.1, 121.6, 79.5, 47.1, 40.1, 24.98, 22.0; HRMS (ESI) calcd for $C_{17}H_{17}BrN_2O_5SNa$ *m/z* $[M + Na]^+$: 462.9934; found: 462.9924. HPLC (Daicel Chiralpak IC, *i*-PrOH/hexane = 15/85, 0.6 mL/min, 230 nm) t_1 = 22.9 min (major), t_2 = 24.7 min (minor).



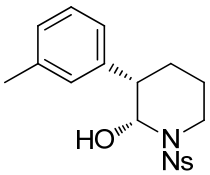
PDA Ch1 230nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.960	593506	14751	50.943	50.513
2	24.716	571529	14451	49.057	49.487
Total		1165035	29203	100.000	100.000



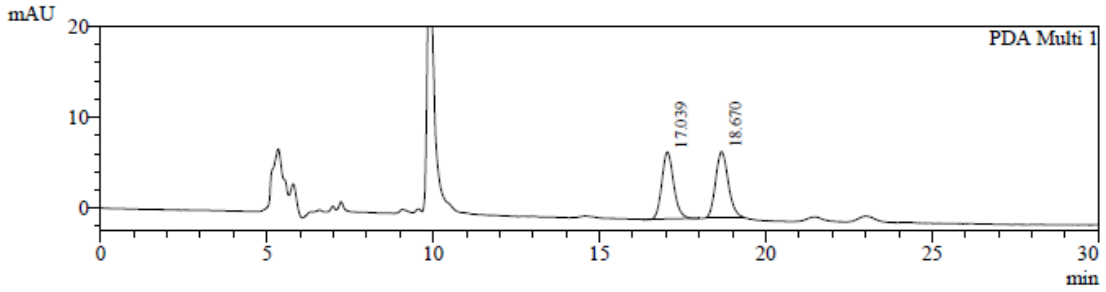
PDA Ch1 230nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.861	7196694	174560	86.248	86.058
2	24.662	1147452	28280	13.752	13.942
Total		8344145	202840	100.000	100.000



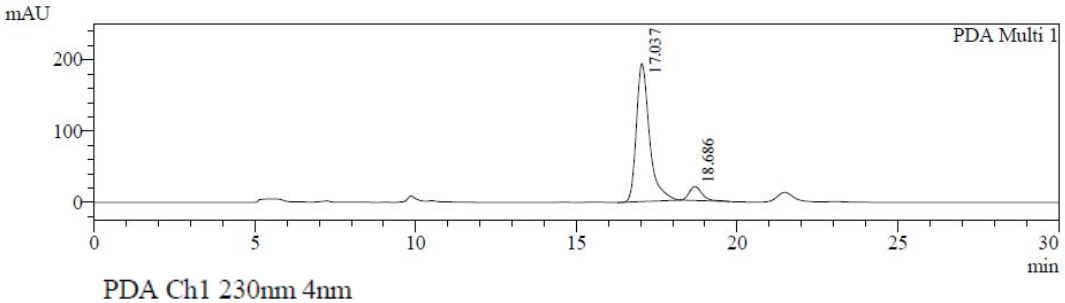
(2*R*,3*R*)- 1-(4-nitrophenylsulfonyl)-3-(*m*-tolyl)piperidin-2-ol (3g)

Yellow oil. $[\alpha]_D^{25}$ +77 (*c* 1.0, $CHCl_3$, 82% ee); IR (film): 3494, 2935, 1529, 1349, 1162, 1091 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 8.31 (d, *J* = 8.8 Hz, 2H), 8.05 (d, *J* = 8.8 Hz, 2H), 7.24 (d, *J* = 7.6 Hz, 1H), 7.12 – 7.03 (m, 3H), 5.64 (s, 1H), 3.70 (d, *J* = 10.9 Hz, 1H), 2.99 (dd, *J* = 16.9, 13.1 Hz, 2H), 2.35 (s, 3H), 2.09 (dd, *J* = 13.0, 3.2 Hz, 1H), 1.95 (d, *J* = 13.7 Hz, 1H), 1.83 – 1.74 (m, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 150.0, 145.3, 140.1, 138.8, 129.2, 128.9, 128.8, 128.4, 124.8, 123.98, 79.9, 47.3, 40.2, 25.0, 21.7, 21.4; HRMS (ESI) calcd for $C_{18}H_{20}N_2O_5SNa$ *m/z* $[M + Na]^+$: 399.0985; found: 399.0977. HPLC (Daicel Chiralpak IC, *i*-PrOH/hexane = 20/80, 0.6 mL/min, 230 nm) t_1 = 17.0 min (major), t_2 = 18.7 min (minor).



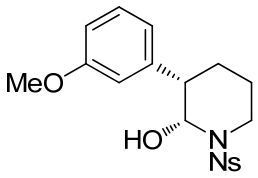
PDA Ch1 230nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.039	180878	7355	49.007	50.450
2	18.670	188208	7223	50.993	49.550
Total		369086	14578	100.000	100.000



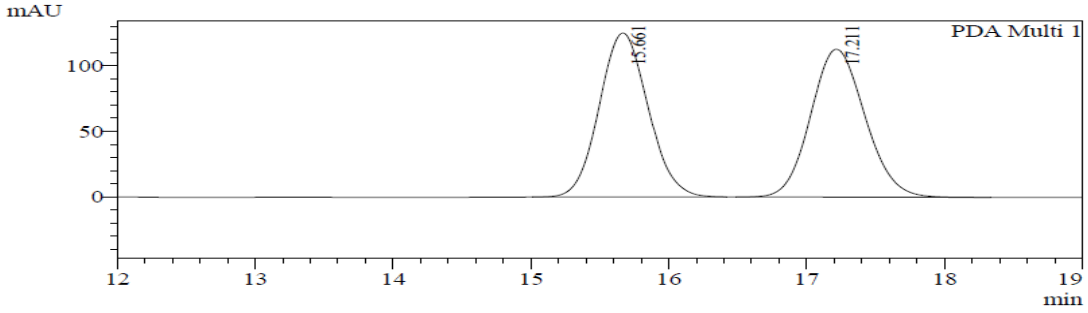
PDA Ch1 230nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.037	5493506	193906	90.924	90.832
2	18.686	548371	19571	9.076	9.168
Total		6041877	213477	100.000	100.000



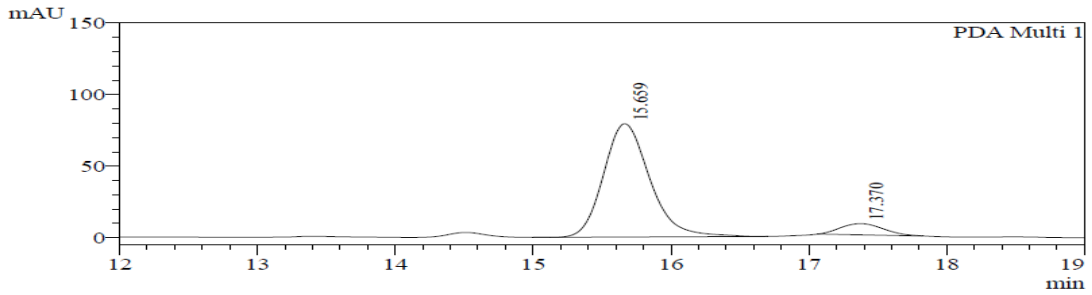
(2*R*,3*R*)- 1-(4-nitrophenylsulfonyl)-3-methoxypiperidin-2-ol (3h)

Yellow oil. $[\alpha]_D^{25}$ +92 (*c* 0.2, $CHCl_3$, 83% ee); IR (film): 3513, 2931, 1529, 1349, 1161, 1090 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.8 Hz, 2H), 8.05 (d, *J* = 8.8 Hz, 2H), 7.28 (d, *J* = 7.9 Hz, 1H), 6.86 – 6.79 (m, 3H), 5.65 (s, 1H), 3.81 (s, 3H), 3.69 (d, *J* = 9.7 Hz, 1H), 3.03 – 2.96 (m, 2H), 2.09 – 2.04 (m, 1H), 1.98 – 1.91 (m, 1H), 1.83 – 1.75 (m, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.0, 150.0, 145.2, 141.8, 130.0, 129.1, 124.0, 120.1, 114.0, 112.7, 79.8, 55.3, 47.5, 40.2, 25.0, 21.8; HRMS (ESI) calcd for $C_{18}H_{20}N_2O_6SNa$ *m/z* $[M + Na]^+$: 415.0934; found: 416.0946. HPLC (Daicel Chiralpak IC, *i*-PrOH/hexane = 40/60, 0.6 mL/min, 230 nm) t_1 = 15.6 min (major), t_2 = 17.3 min (minor).



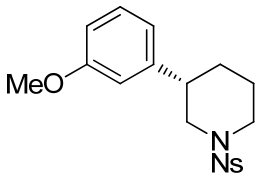
PDA Ch1 230nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.661	3077324	124814	49.888	52.561
2	17.211	3091088	112652	50.112	47.439
Total		6168412	237466	100.000	100.000



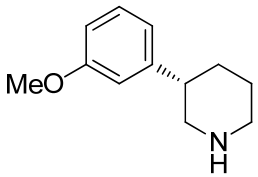
PDA Ch1 230nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.659	1850243	79128	91.628	90.942
2	17.370	169053	7881	8.372	9.058
Total		2019296	87009	100.000	100.000



(*R*)-1-(4-nitrophenylsulfonyl)-3-phenylpiperidine (9)

$[\alpha]_D^{25}$ +215 (*c* 1.0, $CHCl_3$, 83% ee); IR (film): 2936, 1529, 1349, 1170, 1089, 1047, 960 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): ^1H NMR (600 MHz, $CDCl_3$) δ 8.37 (d, *J* = 8.9 Hz, 2H), 7.93 (d, *J* = 8.9 Hz, 2H), 7.25 – 7.21 (m, 1H), 6.79 (ddd, *J* = 8.3, 2.6, 0.6 Hz, 1H), 6.75 (d, *J* = 7.6 Hz, 1H), 6.73 – 6.69 (m, 1H), 3.94 – 3.89 (m, 2H), 3.79 (s, 3H), 2.86 (tt, *J* = 11.7, 3.7 Hz, 1H), 2.35 (td, *J* = 12.0, 2.9 Hz, 1H), 2.28 (t, *J* = 11.4 Hz, 1H), 2.03 – 1.95 (m, 1H), 1.88 (ddd, *J* = 12.9, 6.4, 3.2 Hz, 1H), 1.83 – 1.74 (m, 1H), 1.45 (ddd, *J* = 25.6, 12.6, 3.9 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.8, 150.1, 143.6, 142.5, 129.7, 128.7, 124.3, 119.4, 113.3, 112.0, 55.2, 52.5, 46.4, 42.2, 30.3, 25.0; HRMS (ESI) calcd for $C_{18}H_{20}N_2O_5SNa$ *m/z* $[M + Na]^+$: 399.0985; found: 399.0988.

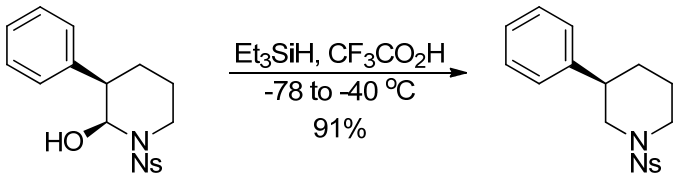


***(S)*-3-(3-methoxyphenyl)piperidine (10)**

To a stirred solution of **9** (18 mg, 0.05 mmol, 1.0 eq) in 0.5 mL of MeCN was added thiophenol (16 μL, 0.25 mmol, 5.0 eq) followed by K_2CO_3 (35 mg, 0.25 mmol, 5.0 eq). After the reaction was stirred for 12 hours, the reaction was quenched with saturated $NaHCO_3$ (2 mL) and extracted with EtOAc (3 x 5 mL). The combined organic layer was dried using $MgSO_4$, filtered, and concentrated under reduced pressure.

$[\alpha]_D^{25}$ +8.0 (*c* 1.0, MeOH, 83% ee); IR (film): 2931, 1601, 1436, 1160, 1089, 1046, 750 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.25 – 7.19 (m, 1H), 6.80 (d, *J* = 7.5 Hz, 1H), 6.78 – 6.71 (m, 2H), 3.80 (s, 3H), 3.25 (dd, *J* = 25.6, 11.8 Hz, 3H), 2.81 (ddd, *J* = 15.1, 11.6, 8.2 Hz, 1H), 2.77 – 2.66 (m, 2H), 2.07 – 1.99 (m, 1H), 1.92 – 1.81 (m, 1H), 1.80 – 1.70 (m, 1H), 1.62 (ddd, *J* = 16.2, 12.9, 3.9 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.71, 145.27, 129.50, 119.37, 113.06, 111.69, 77.21, 77.00, 76.79, 55.17, 52.43, 45.73, 42.90, 31.50, 25.68. HRMS (ESI) calcd for $C_{12}H_{18}NO$ *m/z* $[M + H]^+$: 191.1383; found: 191.1367.

(The data are in full accordance to the literature values in all aspects)[4]

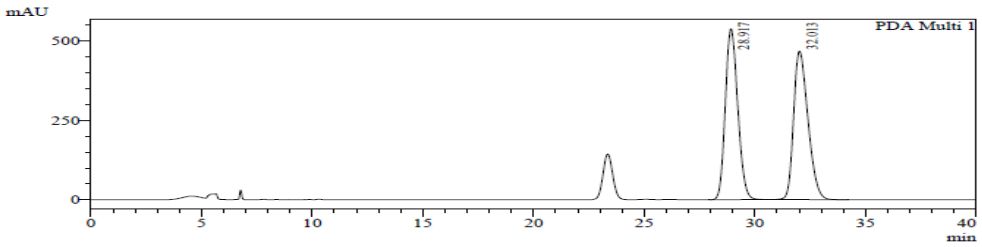


ent-3a **11**

(*R*)-1-(4-nitrophenylsulfonyl)-3-phenylpiperidine (11)

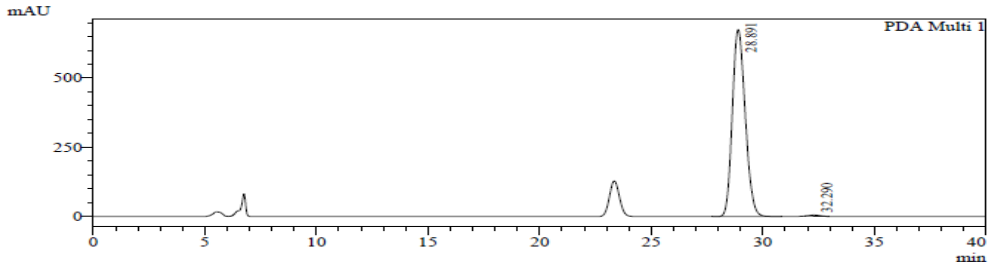
To a stirred solution of **ent-3a** (36 mg, 0.1 mmol, 1.0 eq) in 4 mL of CH_2Cl_2 was added triethylsilane (80 µL, 0.5 mmol, 5.0 eq) at -78°C. The mixture was added trifluoroacetic acid (38 µL, 0.5 mmol, 5.0 eq), stirred and allowed to warm up to room temperature overnight. The reaction was quenched with $NaHCO_3$ and extracted with CH_2Cl_2. The organic phase was dried with $MgSO_4$, filtered and removed under reduced pressure. The residue was purified by column chromatography to yield the desired product **11** as a yellow solid (31 mg, 91%).

$[\alpha]_D^{25}$ −18.0 (*c* 1.0, $CHCl_3$, 99% ee); IR (film): 2935, 1529, 1350, 1168, 1089 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): ^1H NMR (600 MHz, $CDCl_3$) δ 8.37 (d, *J* = 8.7 Hz, 2H), 7.93 (d, *J* = 8.7 Hz, 2H), 7.31 (t, *J* = 7.4 Hz, 2H), 7.25 (d, *J* = 7.4 Hz, 1H), 7.17 (d, *J* = 7.2 Hz, 2H), 3.92 (d, *J* = 11.5 Hz, 2H), 2.92 – 2.85 (m, 1H), 2.35 (td, *J* = 12.0, 2.5 Hz, 1H), 2.29 (t, *J* = 11.4 Hz, 1H), 1.99 (d, *J* = 13.3 Hz, 1H), 1.92 – 1.86 (m, 1H), 1.86 – 1.75 (m, 1H), 1.47 (ddd, *J* = 25.6, 12.7, 3.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 150.13, 142.51, 141.97, 128.72, 127.19, 127.10, 124.33, 52.59, 46.40, 42.17, 30.31, 25.04; HRMS (ESI) calcd for $C_{18}H_{20}N_2O_3S$ *m/z* $[M + Na]^+$: 367.1087; found: 367.1094. HPLC (Daicel Chiralpak IC, *i*-PrOH/hexane = 40/60, 0.6 mL/min, 230 nm) t_1 = 28.9 min (major), t_2 = 32.3 min (minor).



PDA Ch1 230nm 4nm

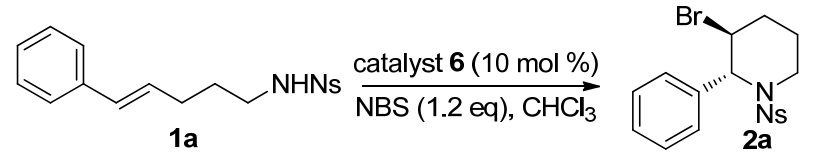
Peak#	Ret. Time	Area	Height	Area %	Height %
1	28.917	21092373	538388	49.934	53.501
2	32.013	21148372	467920	50.066	46.499
Total		42240744	1006308	100.000	100.000



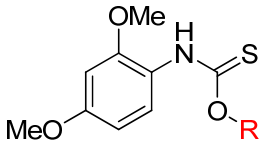
PDA Ch1 230nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	28.891	27190421	675997	99.502	99.420
2	32.290	136141	3941	0.498	0.580
Total		27326562	679938	100.000	100.000

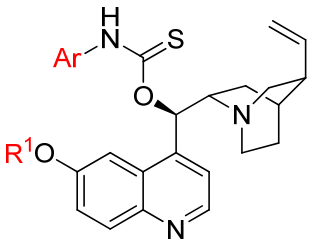
Table S1 Bromoaminocyclization of **1a** using thiocarbamate **6**.



1a **2a**



6a R = cinchonidine
6b R = cinchonine
6c R = quinine
6d R = quinidine

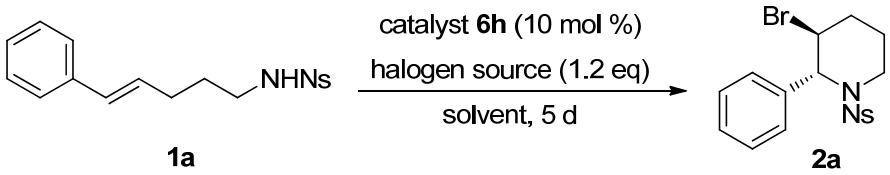


6e Ar = 2,4-$(MeO)_2$-C_6H_3; R^1 = *i*Pr
6f Ar = 2,4-$(MeO)_2$-C_6H_3; R^1 = CPh_3
6g Ar = 2,4-$(MeO)_2$-C_6H_3; R^1 = isoamyl
6h Ar = 2,4-$(MeO)_2$-C_6H_3; R^1 = neopentyl
6j Ar = 2,4,6-$(MeO)_3$-C_6H_2; R^1 = Me
6k Ar = 3,4,5-$(MeO)_3$-C_6H_2; R^1 = Me
6l Ar = 2,4-Cl_2-C_6H_3; R^1 = Me
6m Ar = 2,4-Me_2-C_6H_3; R^1 = Me
6n Ar = 4-(Me_2N)-C_6H_4; R^1 = Me

entry[a]	catalyst	temperature (°C)	time (d)	yield,[b] ee (%)
1	**6a**	-50	3	17, 2
2	**6b**	-50	3	21, 0
3	**6c**	-50	3	15, 46
4	**6d**	-50	3	10, -9
5	**6e**	-62	3	81, 63
6	**6f**	-62	3	67, 68
7	**6g**	-50	3	63, 55
8	**6h**	-50	4	50, 73
9	**6j**	-50	5	NR
10	**6k**	-50	4	NR
11	**6l**	-50	3	NR
12	**6m**	-50	3	NR
13	**6n**	-50	3	NR

[a] Reactions were carried out with **1a** (0.1 mmol), NBS (0.12 mmol), catalyst **6** (0.01 mmol) in $CHCl_3$ (5 mL). [b] Isolated yield.

Table S2 Optimization of the bromoaminocyclization of **1a.**

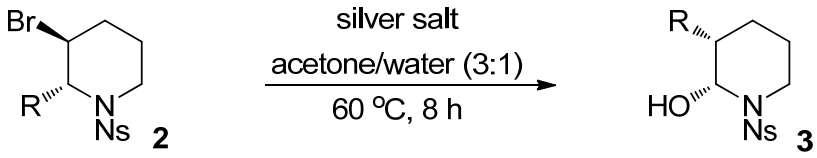


1a **2a**

entry	halogen source	solvent	temperature (°C)	yield,[b] ee (%)
1	NBS	$CHCl_3$	-60	39, 75
2	NBP	$CHCl_3$	-60	78, 86
3	DBH	$CHCl_3$	-60	97, 83
4	NBS	toluene	-60	trace
5	NBP	toluene	-60	trace
6	NBS	$CHCl_3$/PhMe (1:1)	-60	71, 80
7	NBS	$CHCl_3$/hexane (1:1)	-60	89, 86
8	NBP	$CHCl_3$/hexane (1:1)	-78	56, 87
9	NBP	$CHCl_3$/hexane (1:2)	-78	24, 92
10	NBP	$CHCl_3$/hexane (2:1)	-78	18, 88
11	NBP	$CHCl_3$/hexane (2:3)	-78	55, 92
12	NBP	$CHCl_3$/hexane (1:2)	-60	24, 76
13	NBP	$CHCl_3$/hexane (1:2)	-78	21, 92
14	NBP	$CHCl_3$/hexane (2:3)	-60	55, 90
16	DBH	$CHCl_3$/hexane (1:2)	-78	24, 80
17	DBH	$CHCl_3$/hexane (1:1)	-78	85, 90
18	DBH	$CHCl_3$/hexane (2:1)	-78	74, 90
19	DBH	$CHCl_3$/hexane (2:3)	-60	69, 67

[a] Reactions were carried out with **1a** (0.1 mmol), halogen source (0.12 mmol), catalyst **6h** (0.01 mmol) in solvent (5 mL). [b] Isolated yield.

Table S3 Optimization of the silver salt mediated rearrangement of **2.**



entry	silver salt	substrate	R	yield,[b] ee (%)
1	AgOAc	**2a**	Ph	0
2	Ag_2CO_3	**2a**	Ph	0
3	$AgNO_3$	**2a**	Ph	83
4	Ag_3PO_4	**2a**	Ph	0
5	Ag_2SO_4	**2a**	Ph	0
6	AgOTf	**2a**	Ph	43
7	AgOTs	**2a**	Ph	37
8[c]	$Ag(O_2CCF_3)$	**ent-2a**, 99% ee	Ph	86, 99
9	$Ag(O_2CCF_3)$	**2b**, 83% ee	4-F-C_6H_4	83, 83
10	$Ag(O_2CCF_3)$	**2d**, 72% ee	4-Br-C_6H_4	76, 72
11	$Ag(O_2CCF_3)$	**2g**, 86% ee	3-Me-C_6H_4	89, 86
12	$Ag(O_2CCF_3)$	**2h**, 83% ee	3-MeO-C_6H_4	80, 83

[a] Reactions were carried out with **2** (0.1 mmol), silver salt (0.1 mmol) in acetone/water (3:1 v/v, 5 mL) at 60 °C. [b] Isolated yield. [c] **Ent-2a** was used and the corresponding **ent-3a** was isolated as the product.

References

(1) Zhou, L.; Tan, C. K.; Jiang, X.; Chen, F.; Yeung, Y. -Y. *J. Am. Chem. Soc.* **2010**, *132*, 15474–15476.

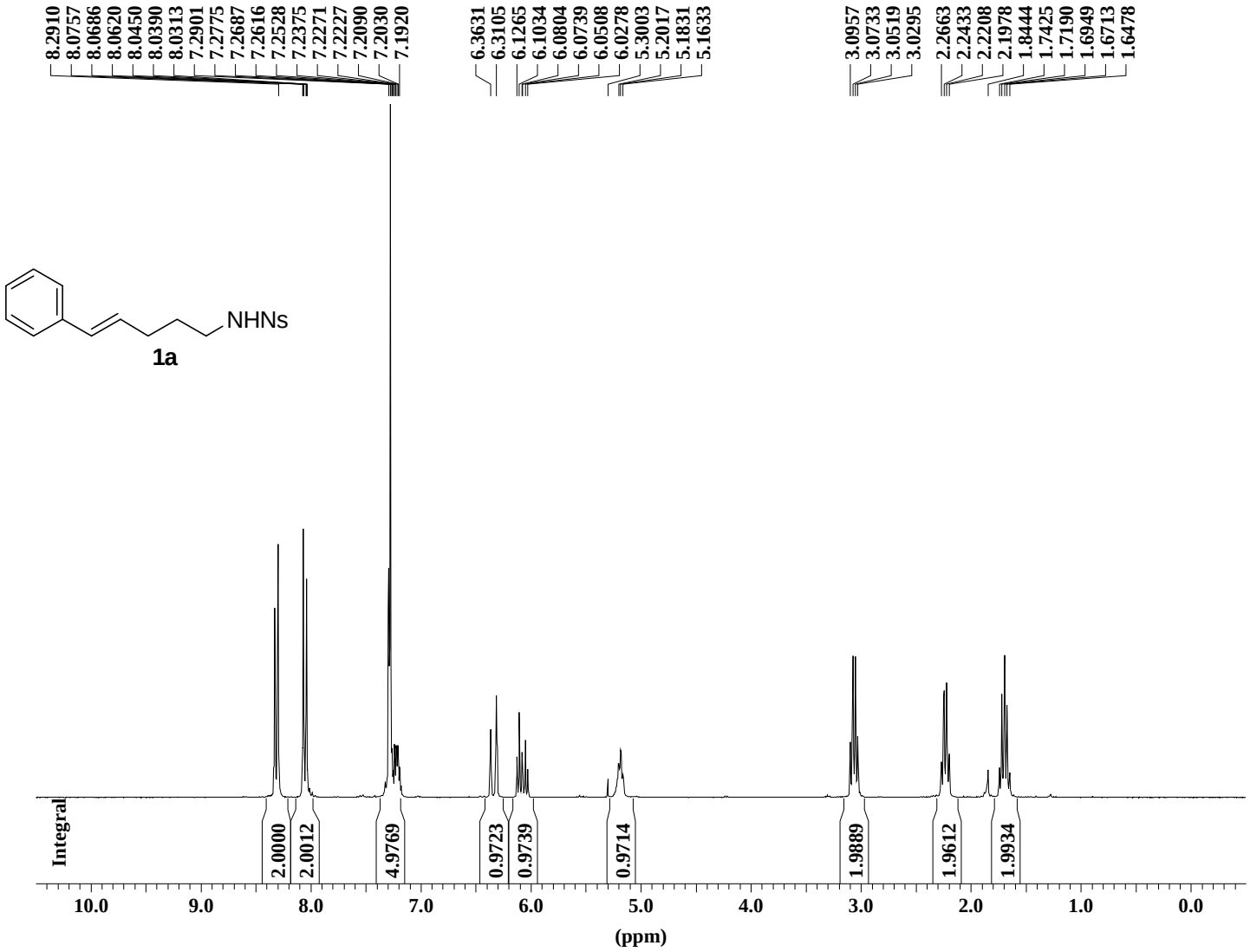
(2) Zhou, L.; Chen, J.; Tan, C. K.; Yeung, Y.-Y. *J. Am. Chem. Soc.* **2011**, *133*, 9164–9167.

(3) Tan, C. K.; Zhou L.; Yeung, Y.-Y. *Org. Lett.* **2011**, *13*, 2738–2741.

(4) Amat, M.; Cantó, M.; Llor, N.; Escolano, C.; Molins, E.; Espinosa, E.; Bosch, J. *J. Org. Chem.,* **2002**, 67, 5343–5351.

1H normal range AC300

z2291D



***** Current Data Parameters *****

NAME	:	oc08zl
EXPNO	:	2
PROCNO	:	1

***** Acquisition Parameters *****

LOCNUC	:	2H
NS	:	8
NUCLEUS	:	off
O1	:	1853.43 Hz
PULPROG	:	zg30
SFO1	:	300.1318534 MHz
SOLVENT	:	CDCl3
SW	:	17.9519 ppm
TD	:	32768
TE	:	296.7 K

***** Processing Parameters *****

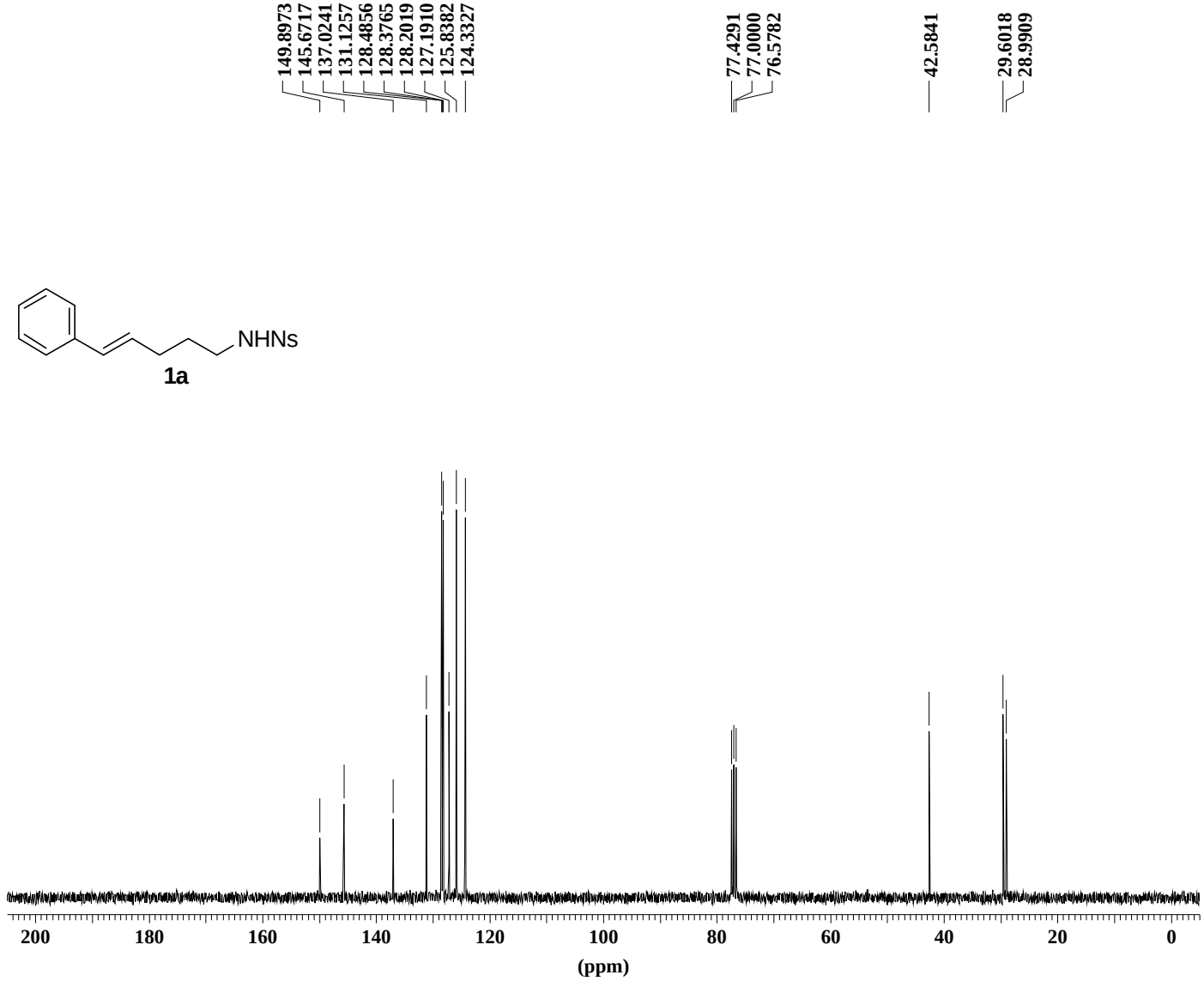
LB	:	0.30 Hz
SF	:	300.1300094 MHz

***** 1D NMR Plot Parameters *****

NUCLEUS	:	off

13C Standard AC300

z2291d



***** Current Data Parameters *****

NAME	:	oc08zl
EXPNO	:	3
PROCNO	:	1

***** Acquisition Parameters *****

LOCNUC	:	2H
NS	:	126
NUCLEUS	:	off
O1	:	7924.11 Hz
PULPROG	:	zgpg30
SFO1	:	75.4756731 MHz
SOLVENT	:	CDCl3
SW	:	238.2968 ppm
TD	:	32768
TE	:	296.9 K

***** Processing Parameters *****

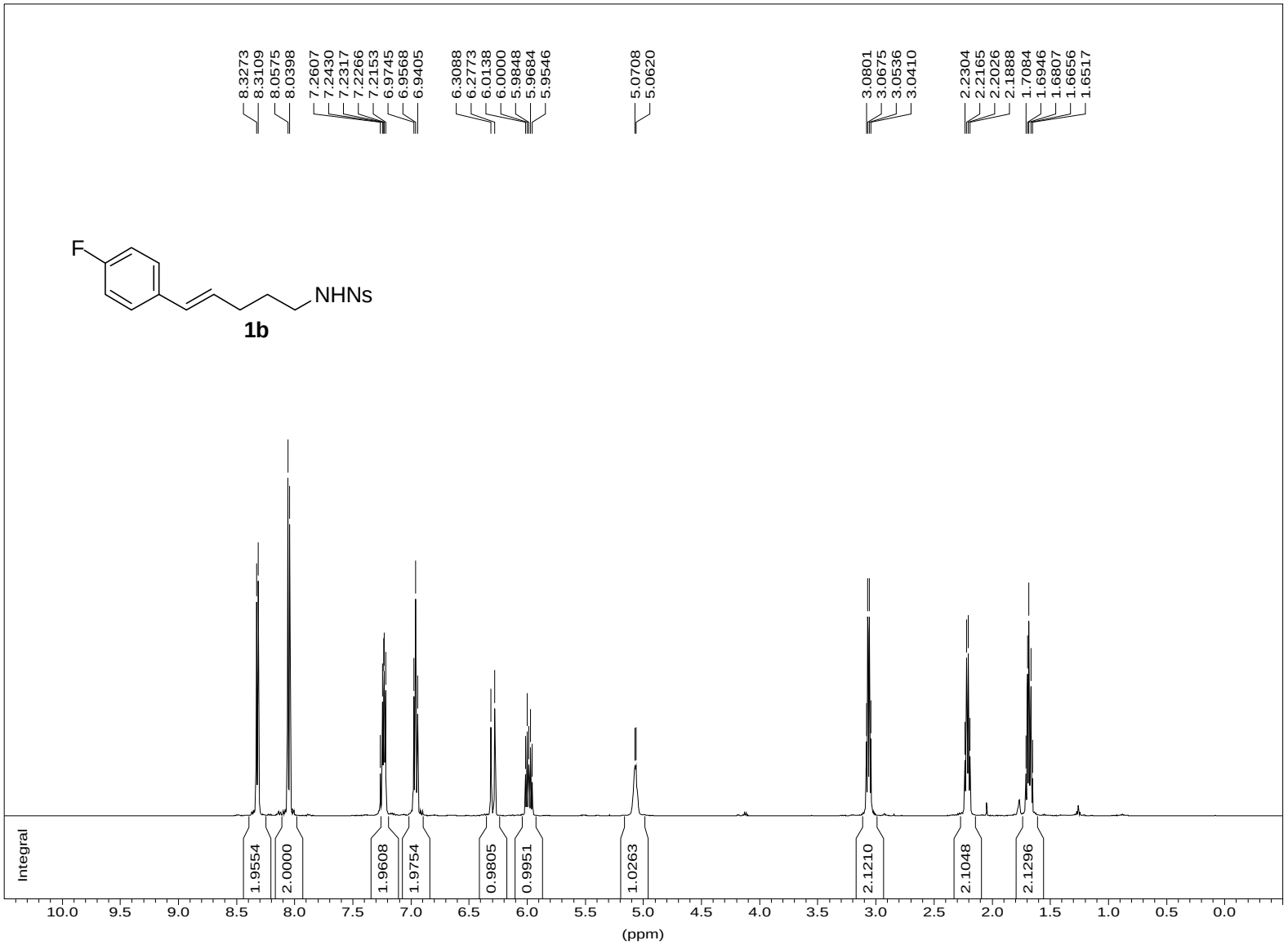
LB	:	1.00 Hz
SF	:	75.4677590 MHz

***** 1D NMR Plot Parameters *****

NUCLEUS	:	off

1H AMX500

3195-2



*** Current Data Parameters ***

NAME	:	zl0818
EXPNO	:	5
PROCNO	:	1

*** Acquisition Parameters ***

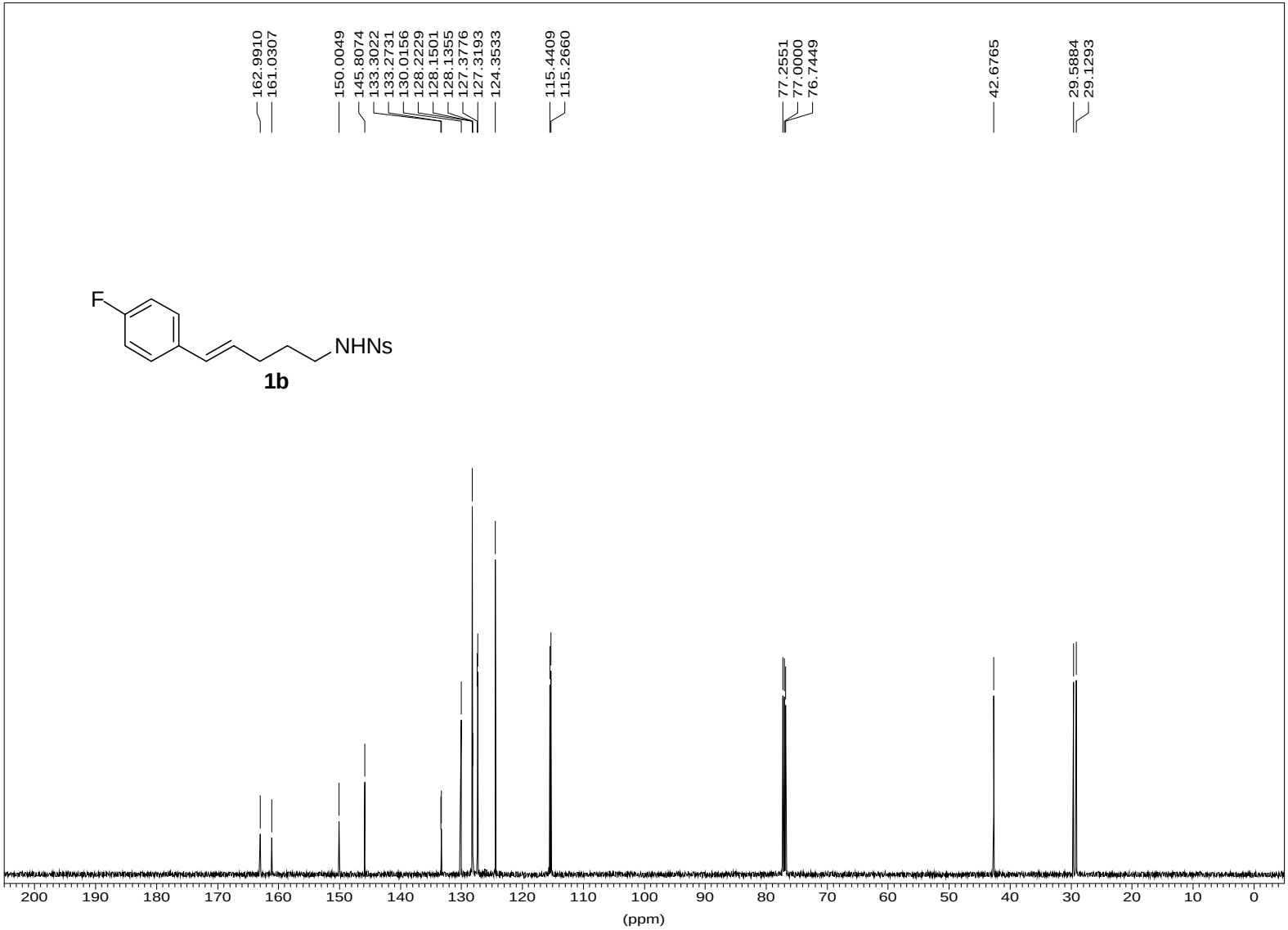
BF1	:	500.1300000 MHz
LOCNUC	:	2H
NS	:	8
O1	:	3088.51 Hz
PULPROG	:	zg30
SFO1	:	500.1330885 MHz
SOLVENT	:	CDCl3
SW	:	20.6557 ppm

*** Processing Parameters ***

LB	:	0.30 Hz
PHC0	:	158.770 degree
PHC1	:	-0.316 degree

13C AMX500

3195-2



*** Current Data Parameters ***

NAME	:	zl0818
EXPNO	:	6
PROCNO	:	1

*** Acquisition Parameters ***

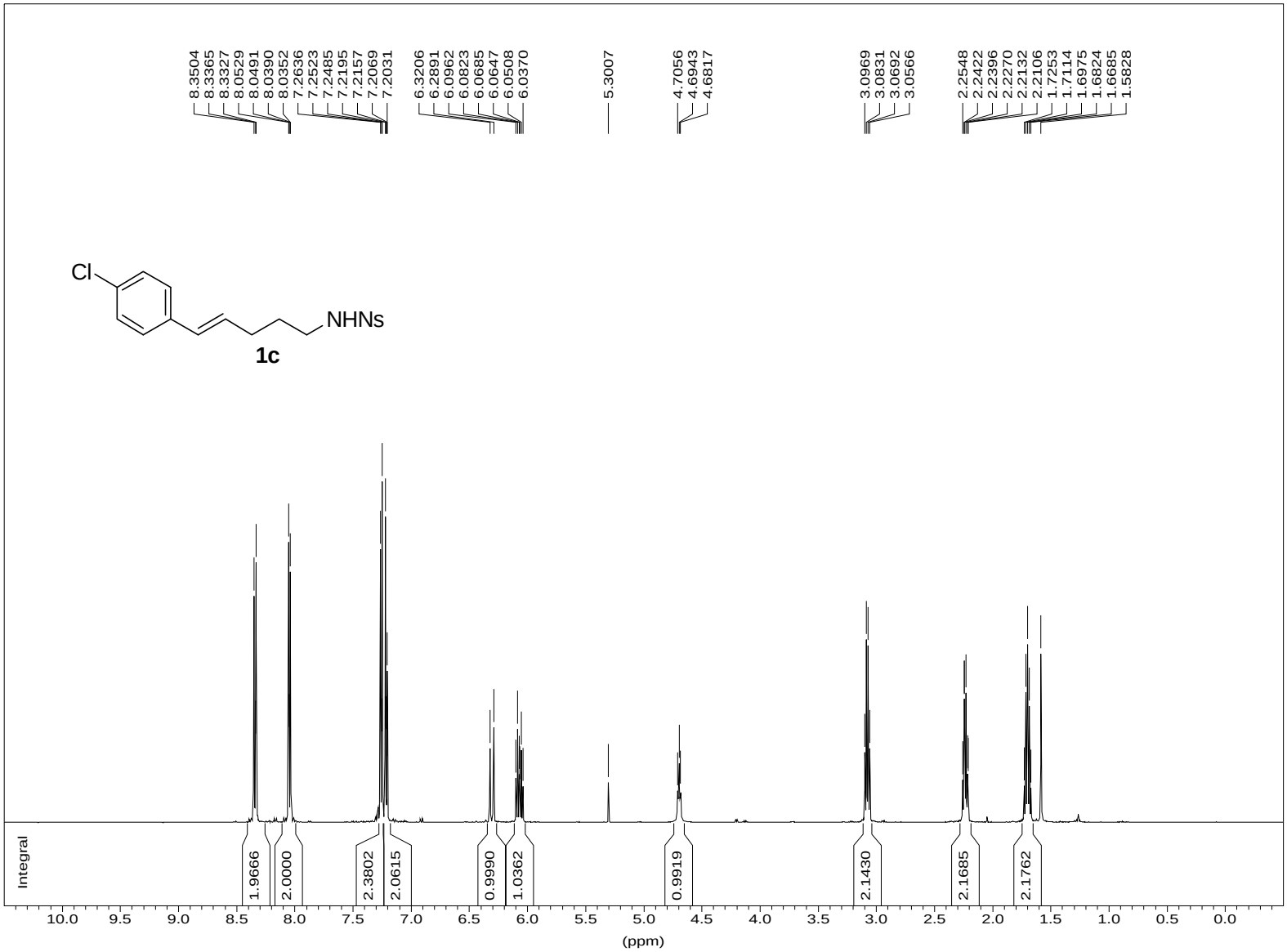
BF1	:	125.7577890 MHz
LOCNUC	:	2H
NS	:	218
O1	:	13204.57 Hz
PULPROG	:	zgpg30
SFO1	:	125.7709936 MHz
SOLVENT	:	CDCl3
SW	:	238.7675 ppm

*** Processing Parameters ***

LB	:	1.00 Hz
PHC0	:	302.066 degree
PHC1	:	39.423 degree

1H AMX500

3195-1



*** Current Data Parameters ***

NAME	:	zl0818
EXPNO	:	1
PROCNO	:	1

*** Acquisition Parameters ***

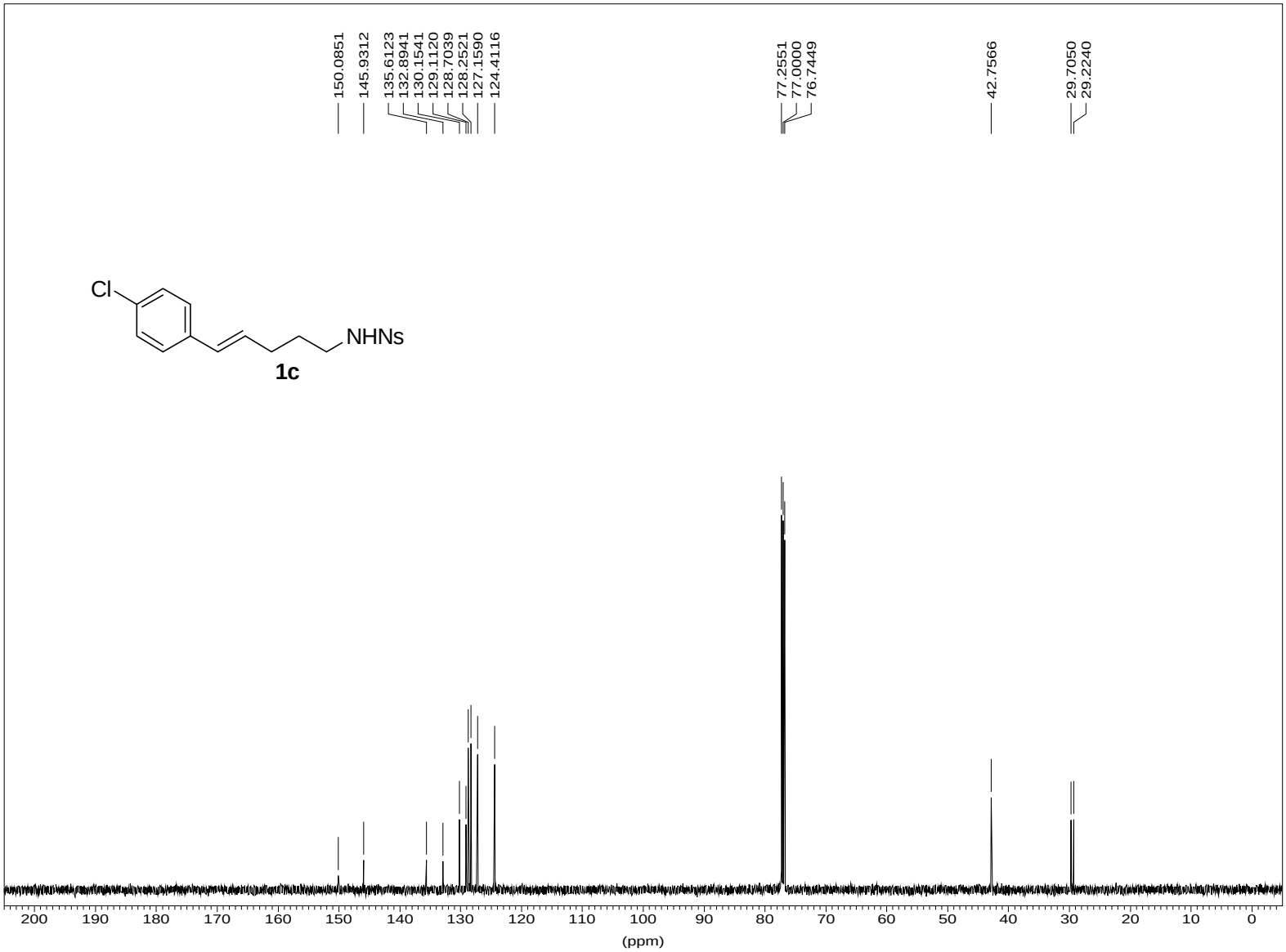
BF1	:	500.1300000 MHz
LOCNUC	:	2H
NS	:	8
O1	:	3088.51 Hz
PULPROG	:	zg30
SFO1	:	500.1330885 MHz
SOLVENT	:	CDCl3
SW	:	20.6557 ppm

*** Processing Parameters ***

LB	:	0.30 Hz
PHC0	:	283.534 degree
PHC1	:	-0.566 degree

13C AMX500

3195-1



*** Current Data Parameters ***

NAME	:	zl0818
EXPNO	:	2
PROCNO	:	1

*** Acquisition Parameters ***

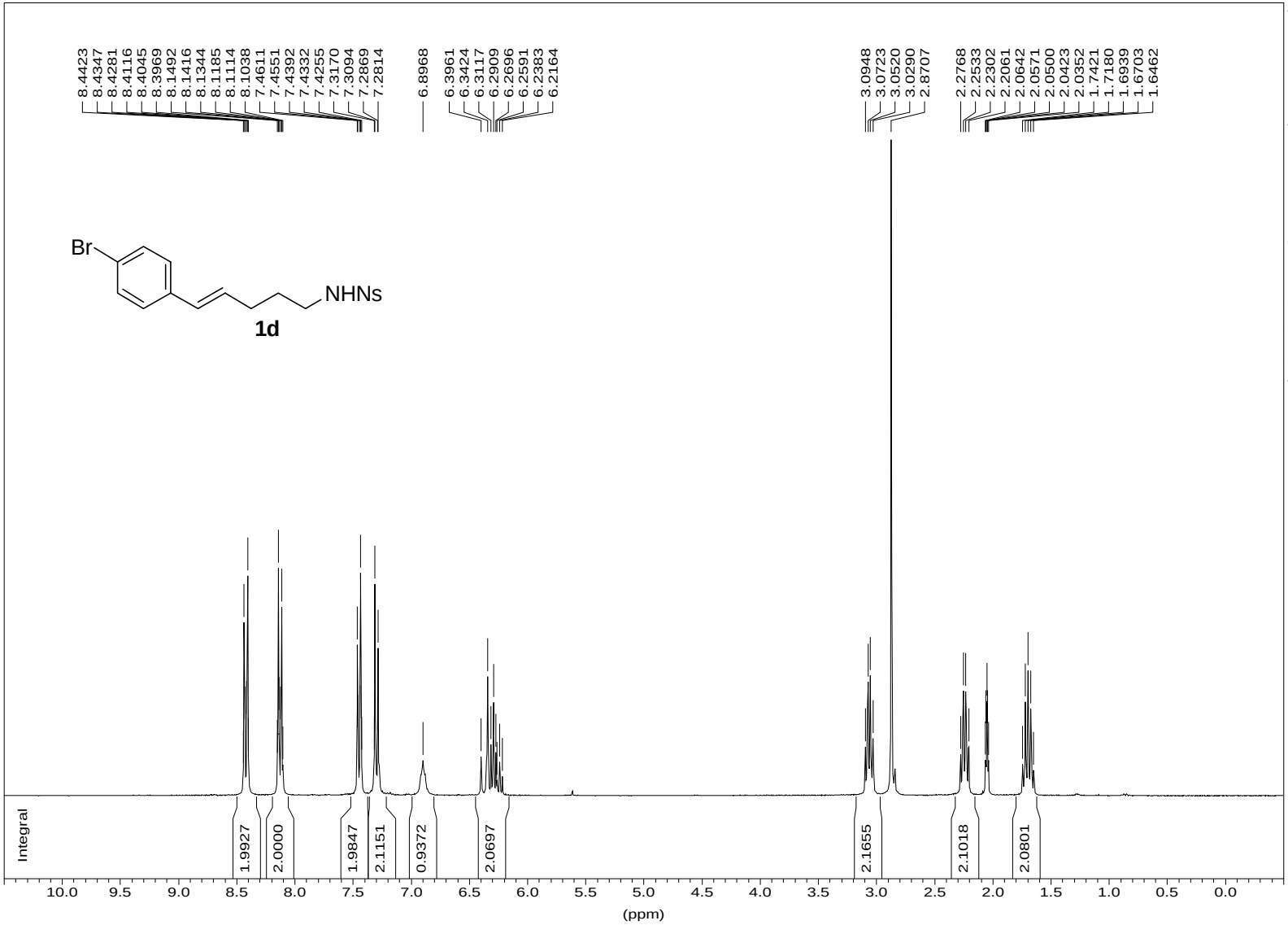
BF1	:	125.7577890 MHz
LOCNUC	:	2H
NS	:	227
O1	:	13204.57 Hz
PULPROG	:	zgpg30
SFO1	:	125.7709936 MHz
SOLVENT	:	CDCl3
SW	:	238.7675 ppm

*** Processing Parameters ***

LB	:	1.00 Hz
PHC0	:	317.407 degree
PHC1	:	20.181 degree

1H normal range AC300

3201-2



*** Current Data Parameters ***

NAME	:	ag27zl
EXPNO	:	7
PROCNO	:	1

*** Acquisition Parameters ***

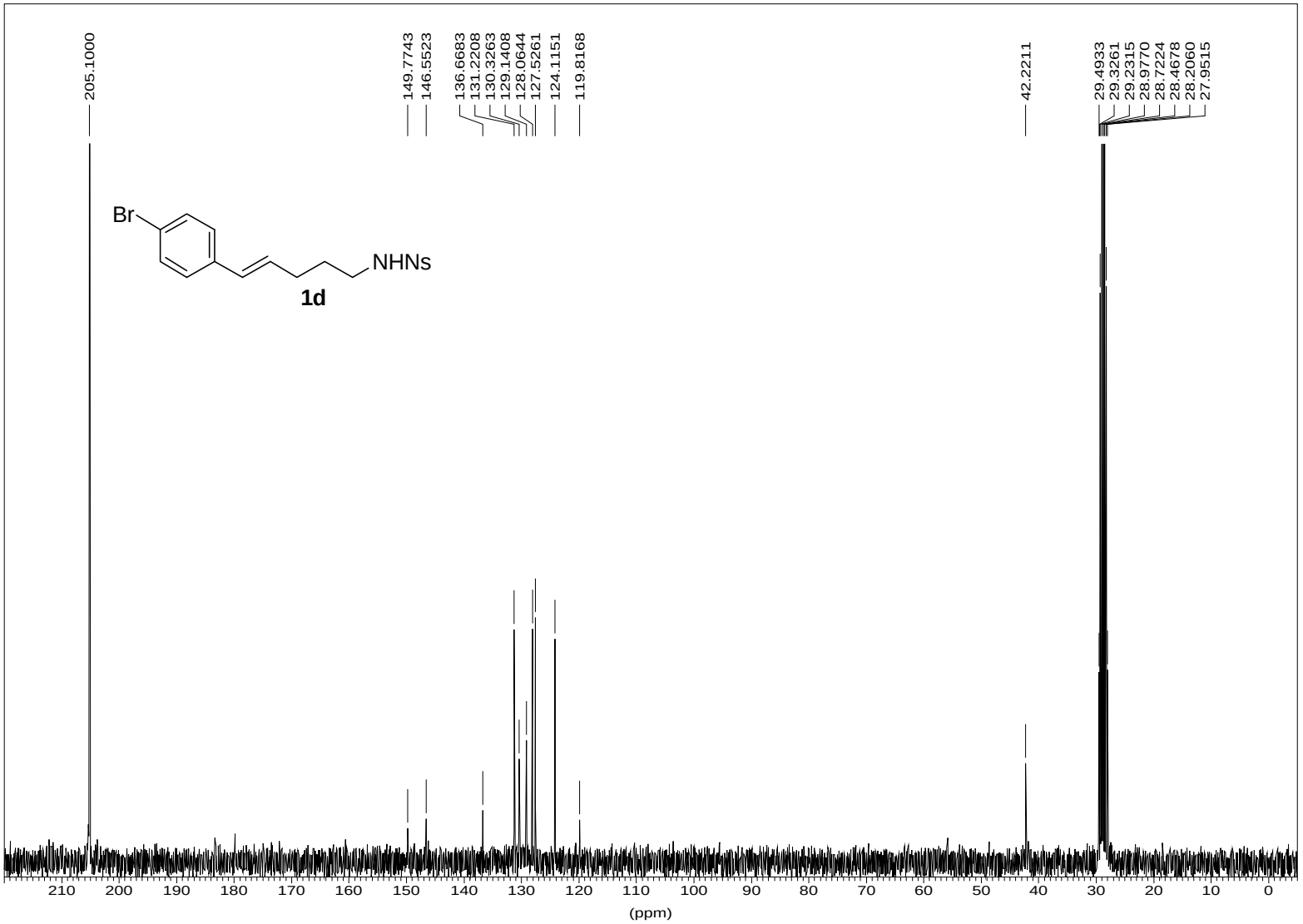
BF1	:	300.1300000 MHz
LOCNUC	:	2H
NS	:	8
O1	:	1853.43 Hz
PULPROG	:	zg30
SFO1	:	300.1318534 MHz
SOLVENT	:	Acetone
SW	:	17.9519 ppm

*** Processing Parameters ***

LB	:	0.30 Hz
PHC0	:	14.375 degree
PHC1	:	-2.633 degree

13C Standard AC300

3201-2



*** Current Data Parameters ***

NAME	:	ag27zl
EXPNO	:	8
PROCNO	:	1

*** Acquisition Parameters ***

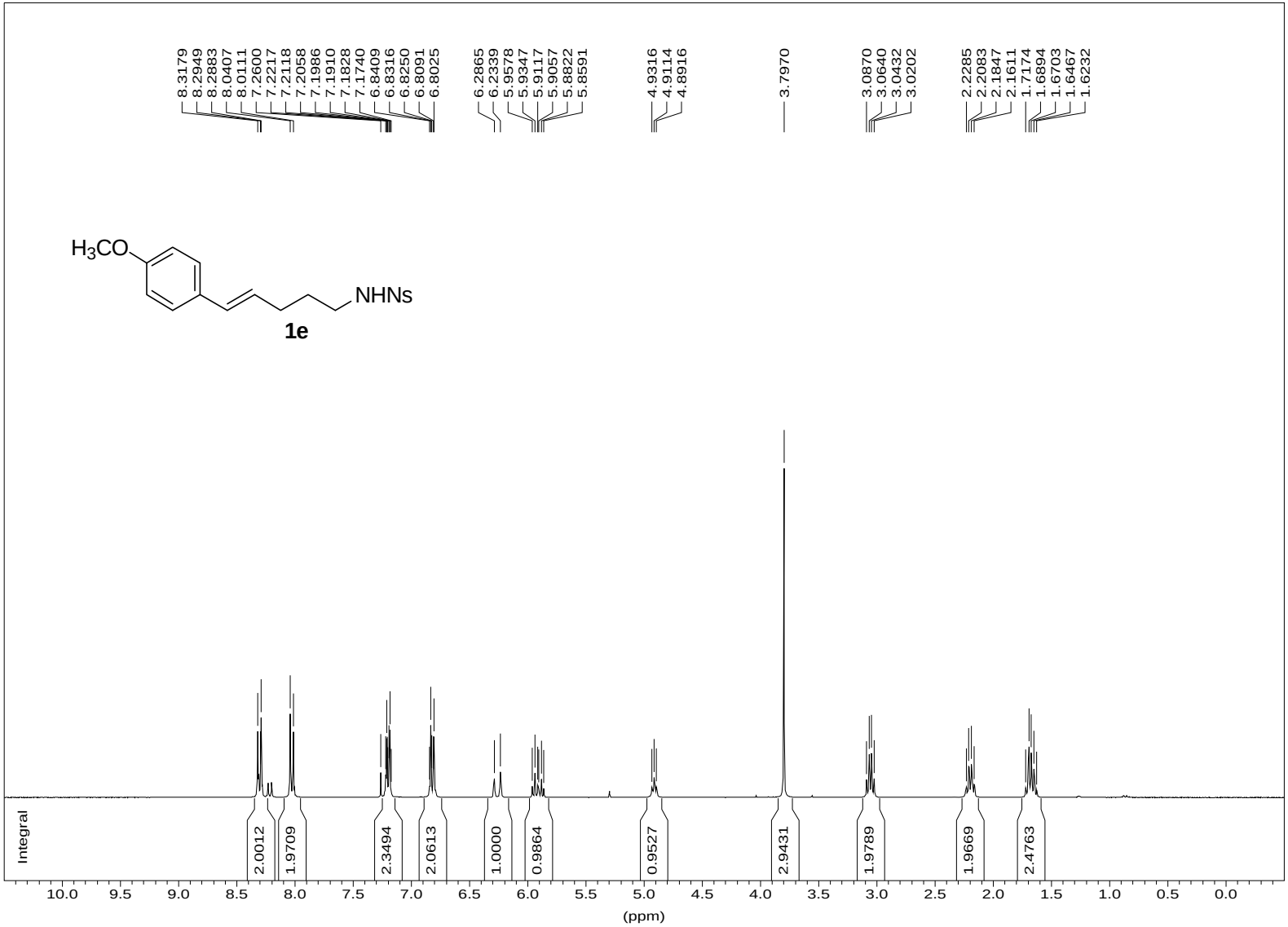
BF1	:	75.4677490 MHz
LOCNUC	:	2H
NS	:	226
O1	:	7924.11 Hz
PULPROG	:	zgpg30
SFO1	:	75.4756731 MHz
SOLVENT	:	CDCl3
SW	:	238.2968 ppm

*** Processing Parameters ***

LB	:	1.00 Hz
PHC0	:	5.911 degree
PHC1	:	3.509 degree

1H normal range AC300

3201-4



*** Current Data Parameters ***

NAME	:	ag27zl
EXPNO	:	3
PROCNO	:	1

*** Acquisition Parameters ***

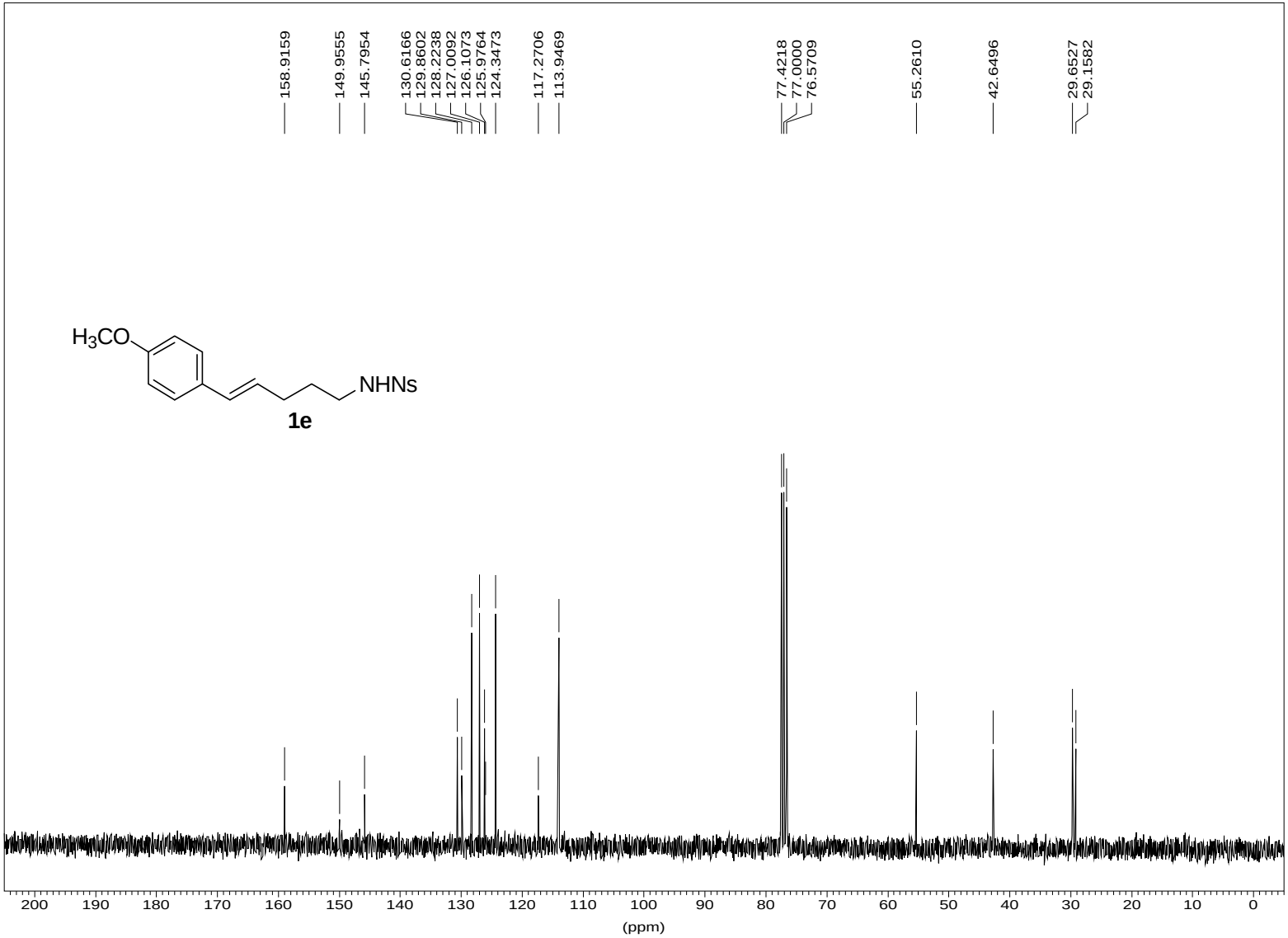
BF1	:	300.1300000 MHz
LOCNUC	:	2H
NS	:	8
O1	:	1853.43 Hz
PULPROG	:	zg30
SFO1	:	300.1318534 MHz
SOLVENT	:	CDCl3
SW	:	17.9519 ppm

*** Processing Parameters ***

LB	:	0.30 Hz
PHC0	:	18.076 degree
PHC1	:	-0.696 degree

13C Standard AC300

3201-4



*** Current Data Parameters ***

NAME	:	ag27zl
EXPNO	:	4
PROCNO	:	1

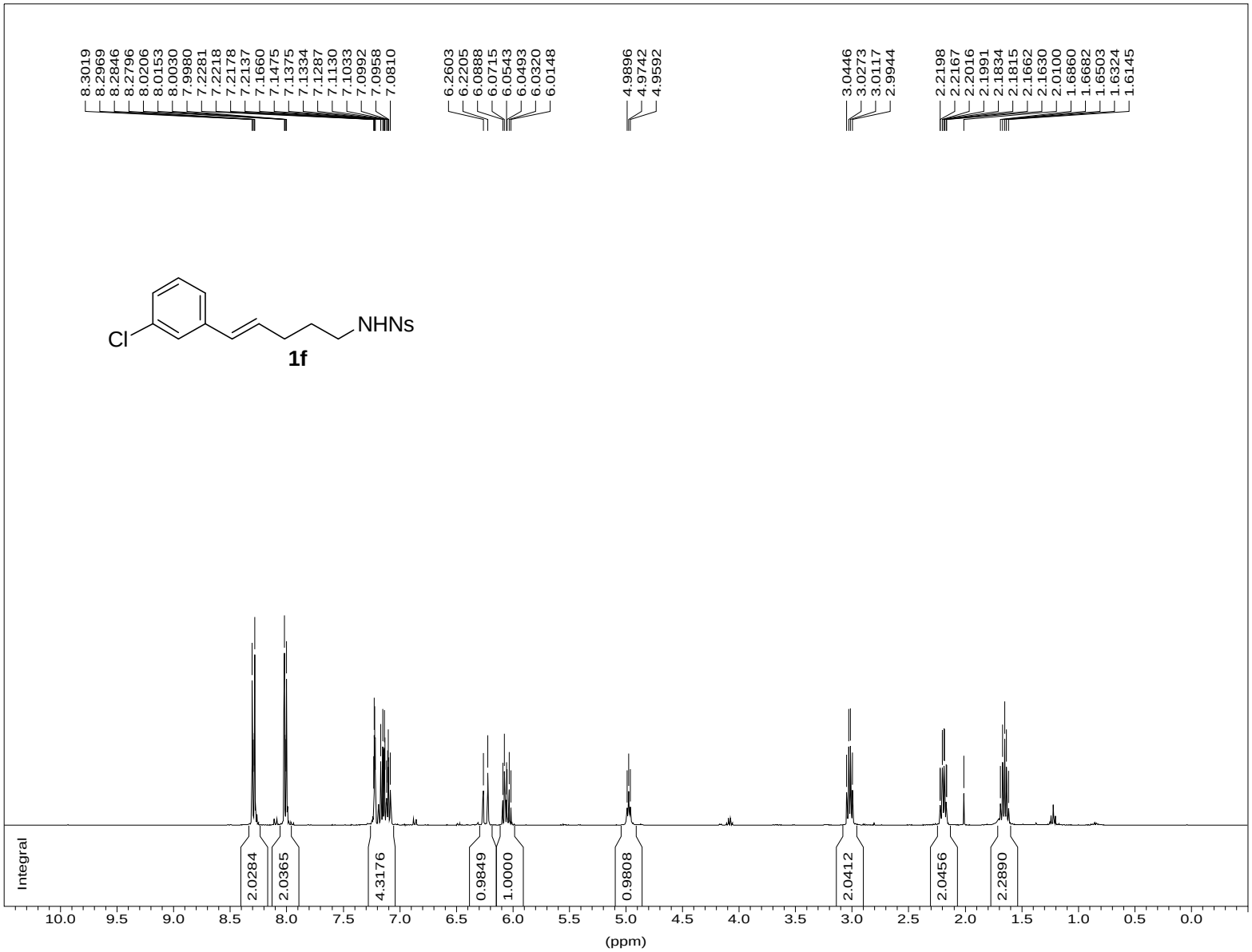
*** Acquisition Parameters ***

BF1	:	75.4677490 MHz
LOCNUC	:	2H
NS	:	239
O1	:	7924.11 Hz
PULPROG	:	zgpg30
SFO1	:	75.4756731 MHz
SOLVENT	:	CDCl3
SW	:	238.2968 ppm

*** Processing Parameters ***

LB	:	1.00 Hz
PHC0	:	29.870 degree
PHC1	:	-32.755 degree

3201-5



*** Current Data Parameters ***

NAME	:	aug31zl
EXPNO	:	4
PROCNO	:	1

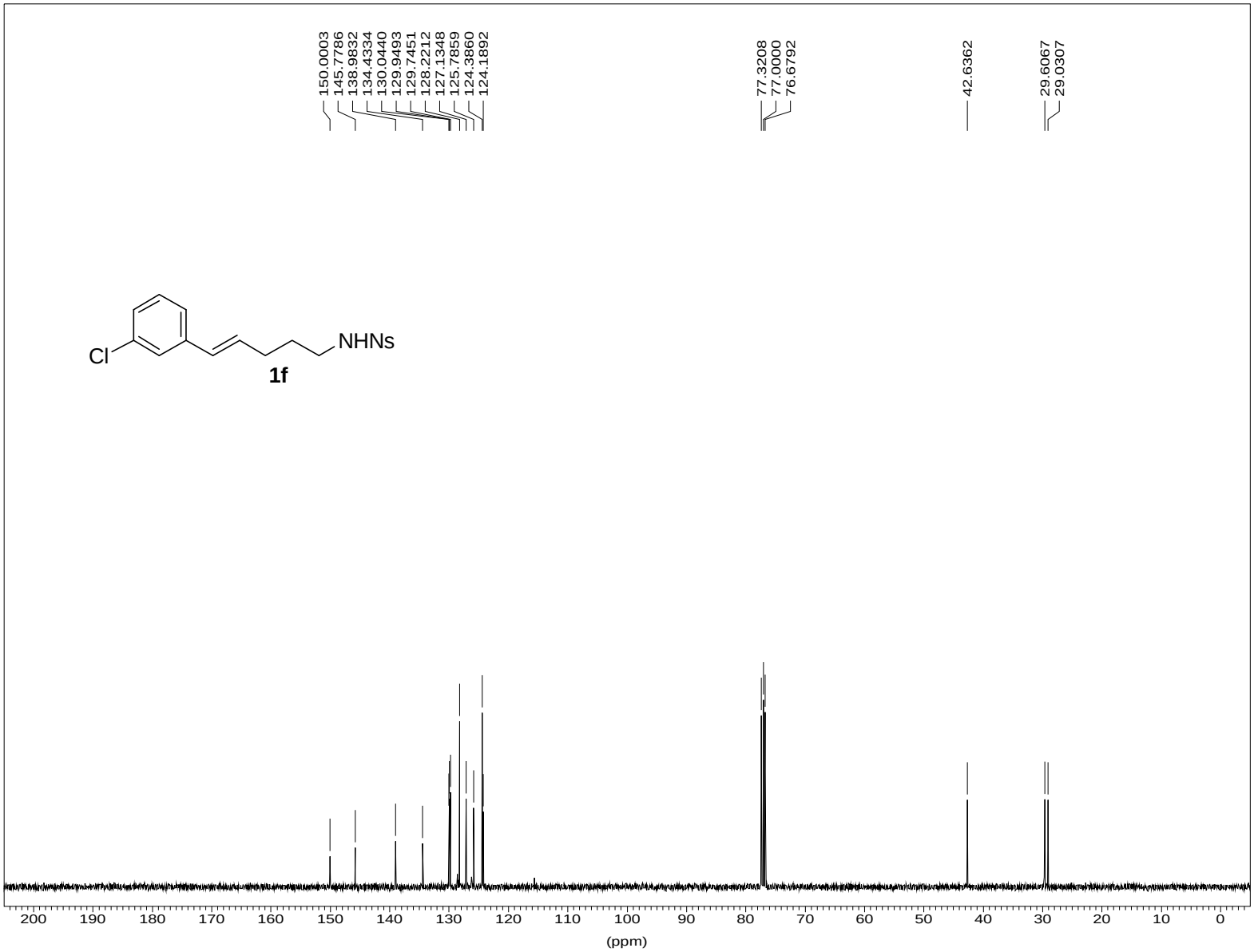
*** Acquisition Parameters ***

BF1	:	400.1300000 MHz
LOCNUC	:	2H
NS	:	8
O1	:	2470.97 Hz
PULPROG	:	zg30
SFO1	:	400.1324710 MHz
SOLVENT	:	CDCl3
SW	:	20.5524 ppm

*** Processing Parameters ***

LB	:	0.30 Hz
PHC0	:	-51.409 degree
PHC1	:	-14.848 degree

3201-5



*** Current Data Parameters ***

NAME	:	aug31zl
EXPNO	:	5
PROCNO	:	1

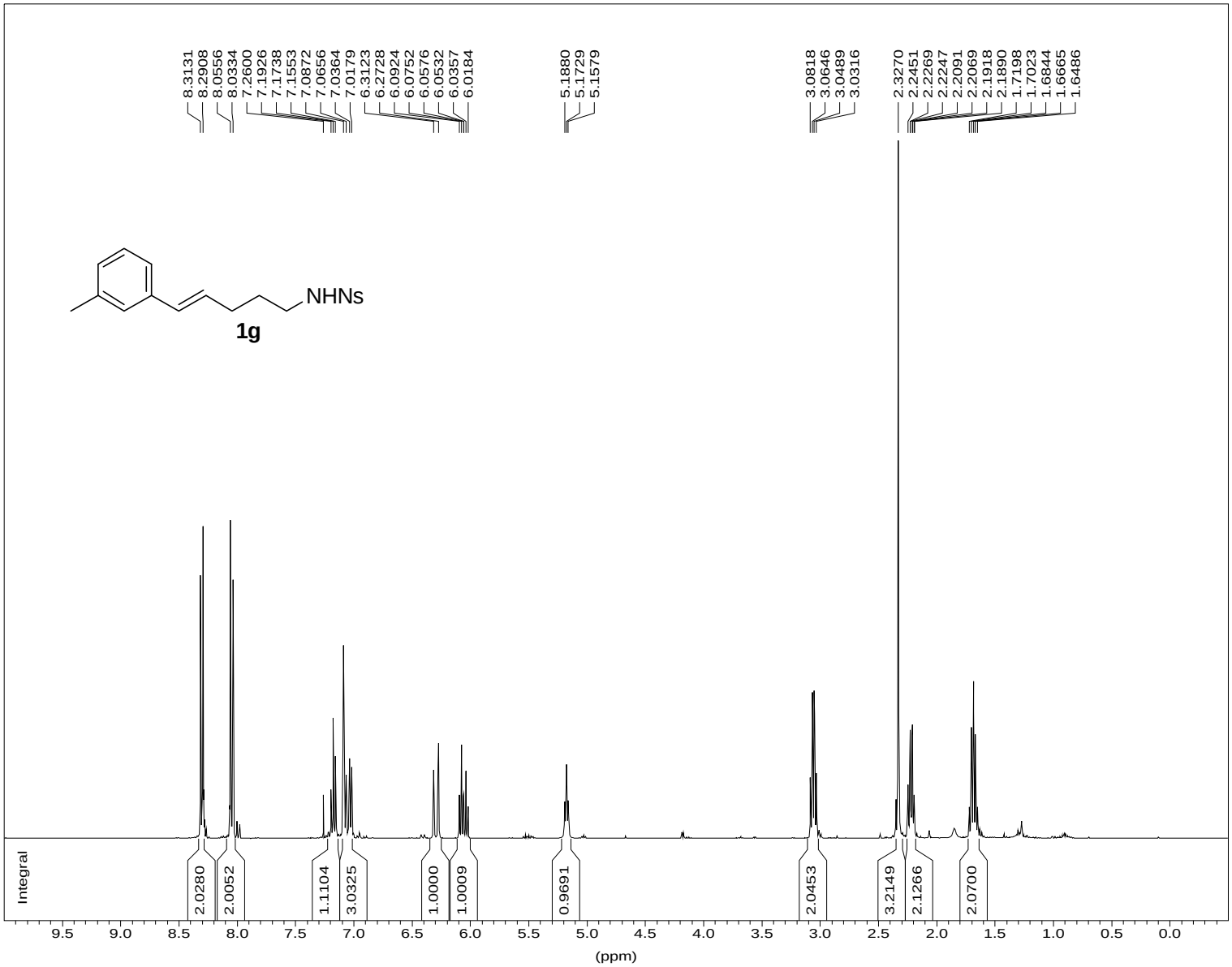
*** Acquisition Parameters ***

BF1	:	100.6127690 MHz
LOCNUC	:	2H
NS	:	93
O1	:	11067.40 Hz
PULPROG	:	zgpg30
SFO1	:	100.6238364 MHz
SOLVENT	:	CDCl3
SW	:	238.8943 ppm

*** Processing Parameters ***

LB	:	1.00 Hz
PHC0	:	95.581 degree
PHC1	:	-67.568 degree

3201-3



*** Current Data Parameters ***

NAME	:	aug26zl
EXPNO	:	2
PROCNO	:	1

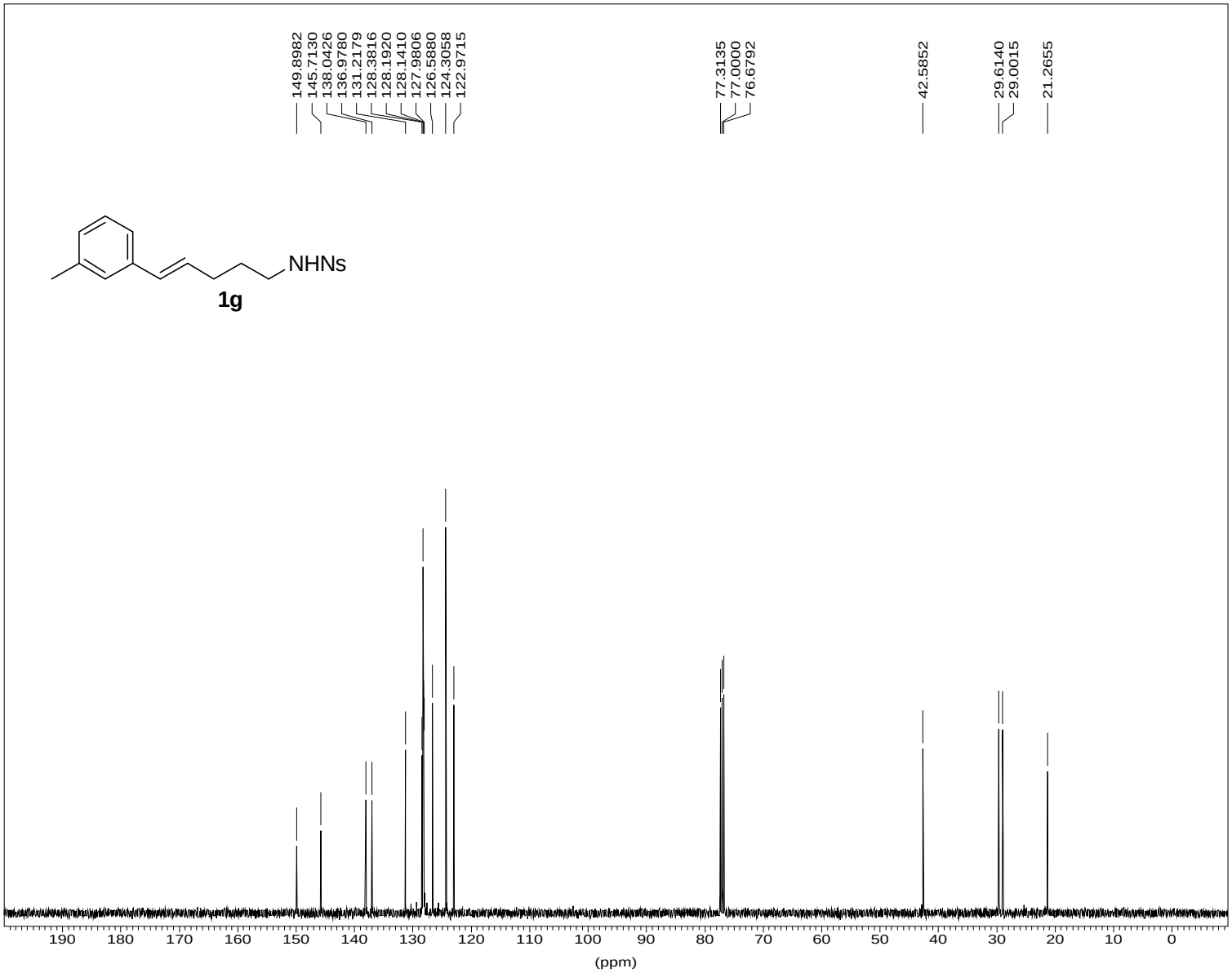
*** Acquisition Parameters ***

BF1	:	400.1300000 MHz
LOCNUC	:	2H
NS	:	8
O1	:	2470.97 Hz
PULPROG	:	zg30
SFO1	:	400.1324710 MHz
SOLVENT	:	CDCl3
SW	:	20.5524 ppm

*** Processing Parameters ***

LB	:	0.30 Hz
PHC0	:	-43.026 degree
PHC1	:	-16.392 degree

3201-3



*** Current Data Parameters ***

NAME	:	aug26zl
EXPNO	:	3
PROCNO	:	1

*** Acquisition Parameters ***

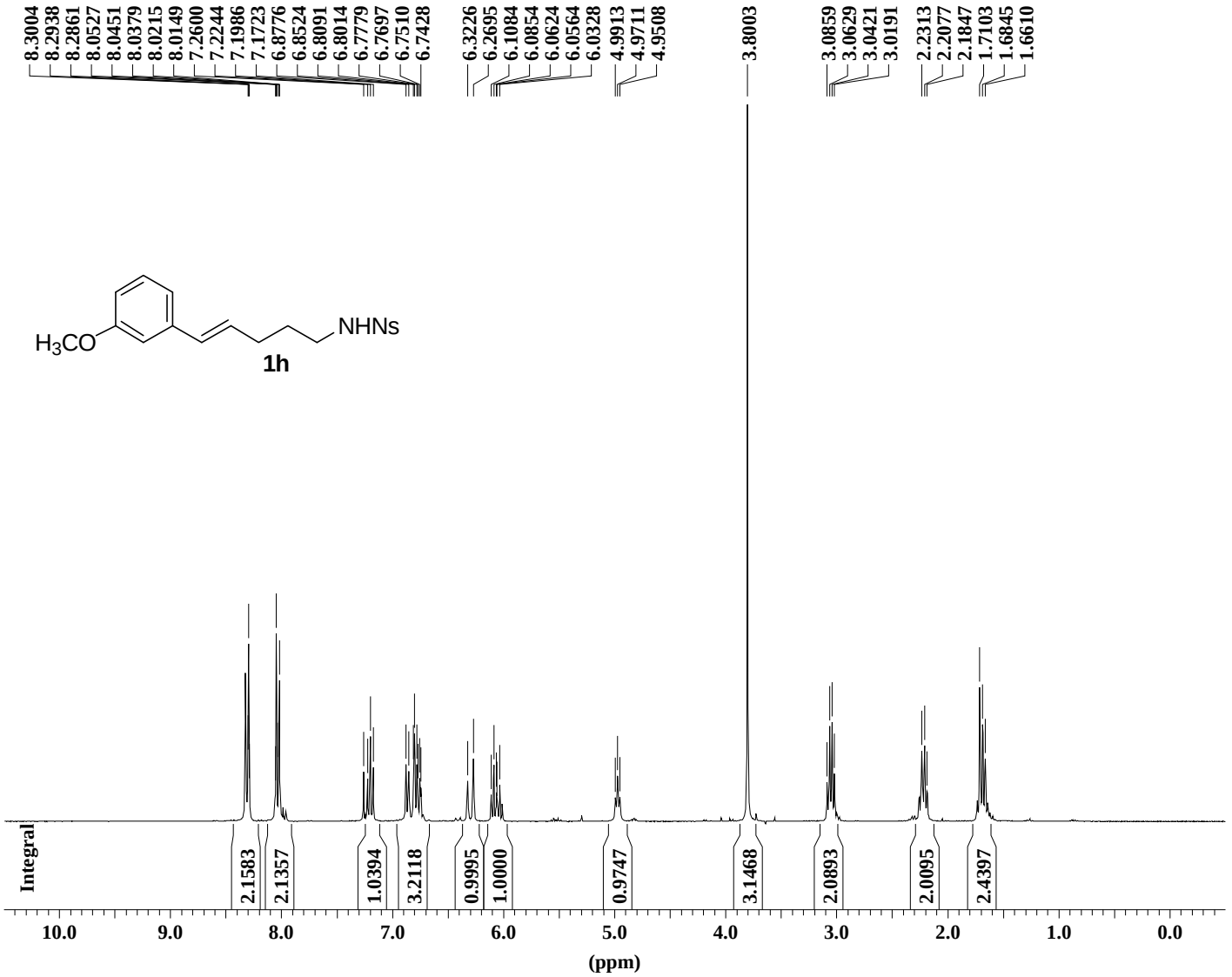
BF1	:	100.6127690 MHz
LOCNUC	:	2H
NS	:	45
O1	:	11067.40 Hz
PULPROG	:	zgpg30
SFO1	:	100.6238364 MHz
SOLVENT	:	CDCl3
SW	:	238.8943 ppm

*** Processing Parameters ***

LB	:	1.00 Hz
PHC0	:	97.699 degree
PHC1	:	-59.040 degree

1H normal range AC300

3201-6



*** Current Data Parameters ***

NAME	:	se01zl
EXPNO	:	1
PROCNO	:	1

*** Acquisition Parameters ***

LOCNUC	:	2H
NS	:	8
NUCLEUS	:	off
O1	:	1853.43 Hz
PULPROG	:	zg30
SFO1	:	300.1318534 MHz
SOLVENT	:	CDCl3
SW	:	17.9519 ppm
TD	:	32768
TE	:	296.9 K

*** Processing Parameters ***

LB	:	0.30 Hz
SF	:	300.1300120 MHz

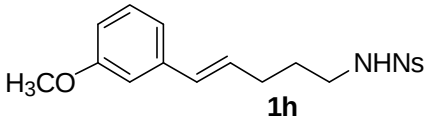
*** 1D NMR Plot Parameters ***

NUCLEUS	:	off

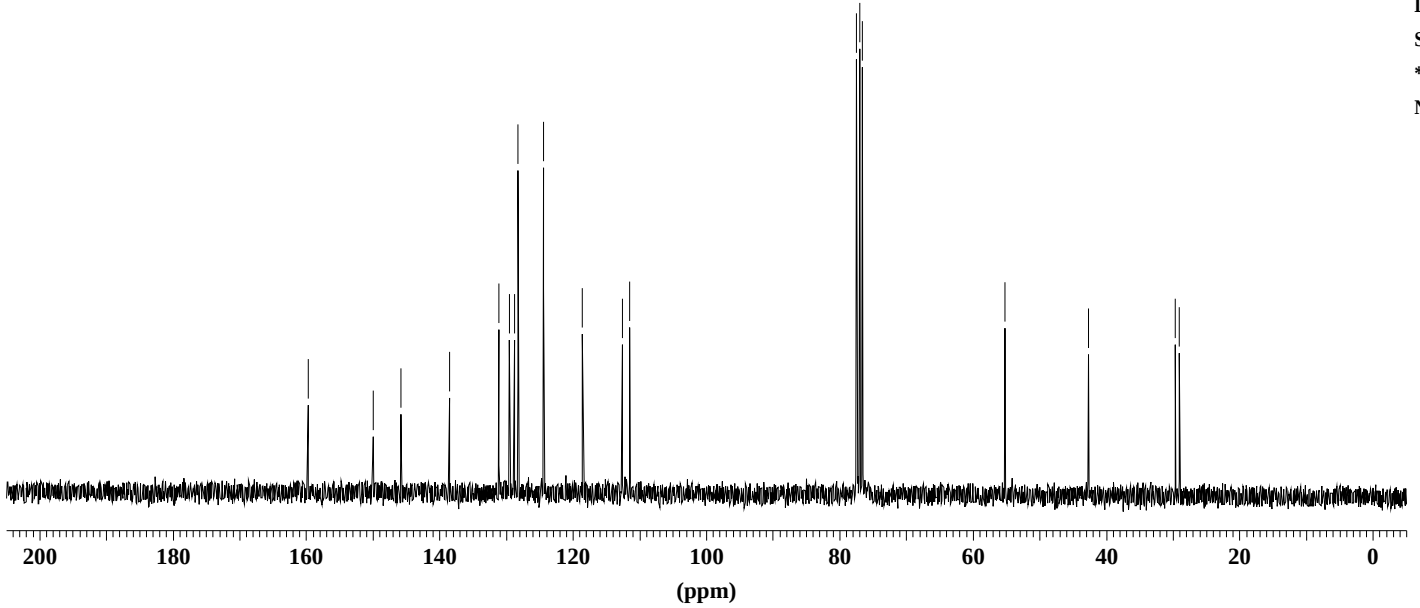
13C Standard AC300

3201-6

159.7377
149.9628
145.7517
138.5296
131.1039
129.5111
128.7474
128.2165
124.3618
118.5507
112.6086
111.4813
77.4218
77.0000
76.5782
55.1592
42.6278
29.6164
29.0200



1h



***** Current Data Parameters *****

NAME	:	se01zl
EXPNO	:	2
PROCNO	:	1

***** Acquisition Parameters *****

LOCNUC	:	2H
NS	:	426
NUCLEUS	:	off
O1	:	7924.11 Hz
PULPROG	:	zgpg30
SFO1	:	75.4756731 MHz
SOLVENT	:	CDCl3
SW	:	238.2968 ppm
TD	:	32768
TE	:	296.9 K

***** Processing Parameters *****

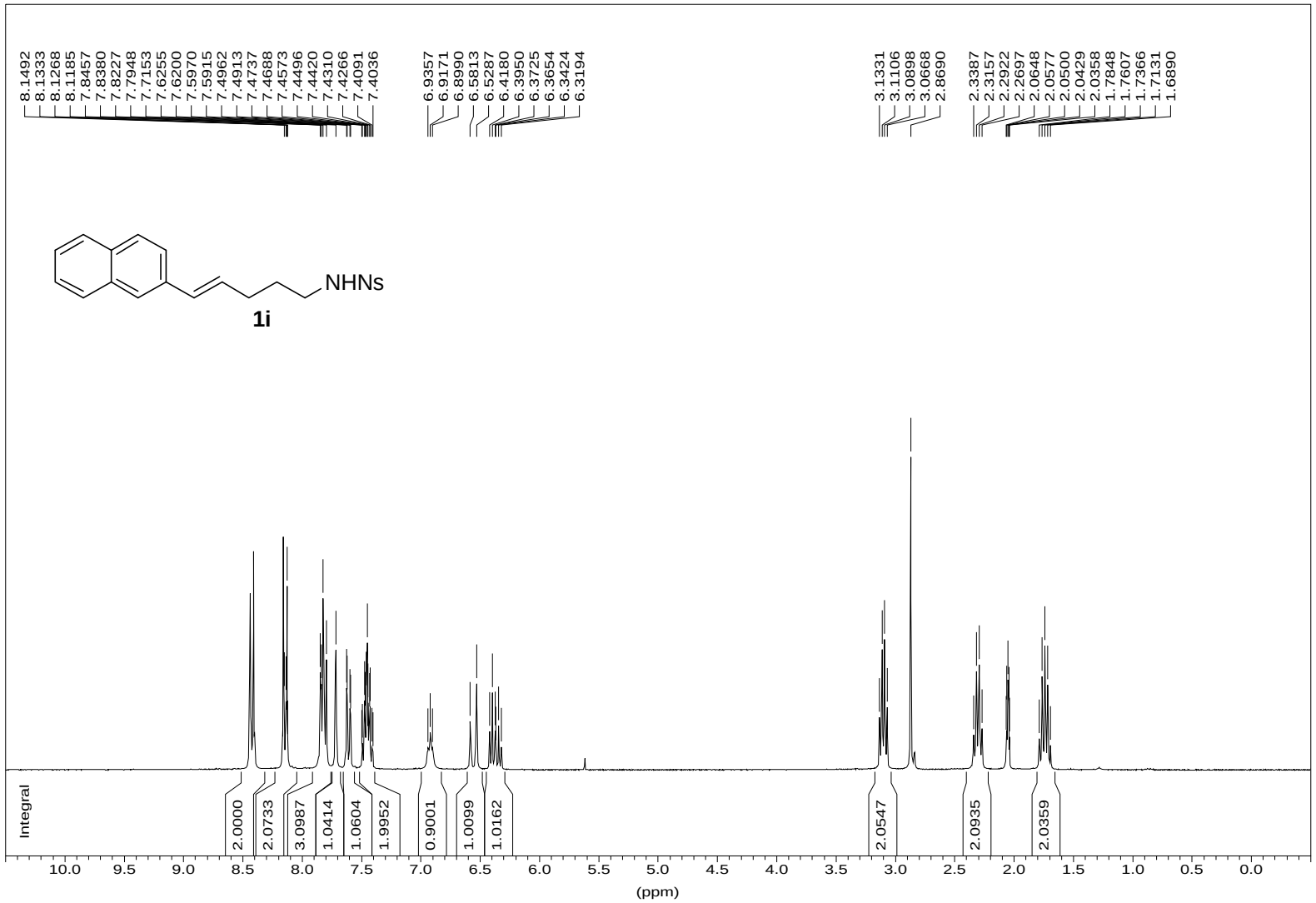
LB	:	1.00 Hz
SF	:	75.4677560 MHz

***** 1D NMR Plot Parameters *****

NUCLEUS	:	off

1H normal range AC300

2-naph



*** Current Data Parameters ***

NAME	:	se14zl
EXPNO	:	5
PROCNO	:	1

*** Acquisition Parameters ***

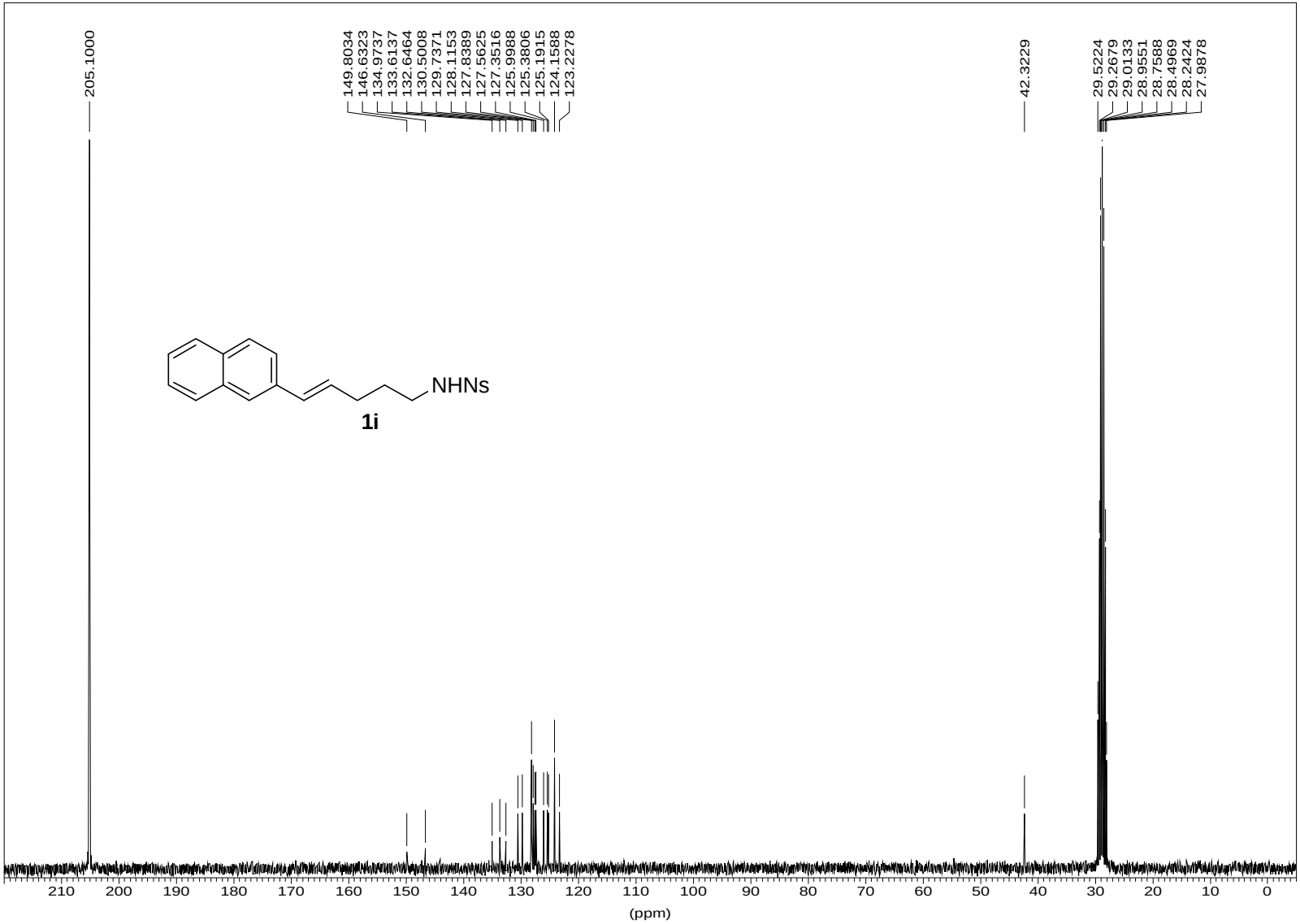
BF1	:	300.1300000 MHz
LOCNUC	:	2H
NS	:	8
O1	:	1853.43 Hz
PULPROG	:	zg30
SFO1	:	300.1318534 MHz
SOLVENT	:	Acetone
SW	:	17.9519 ppm

*** Processing Parameters ***

LB	:	0.30 Hz
PHC0	:	18.514 degree
PHC1	:	-2.218 degree

13C Standard AC300

2-naph



*** Current Data Parameters ***

NAME	:	se14zl
EXPNO	:	6
PROCNO	:	1

*** Acquisition Parameters ***

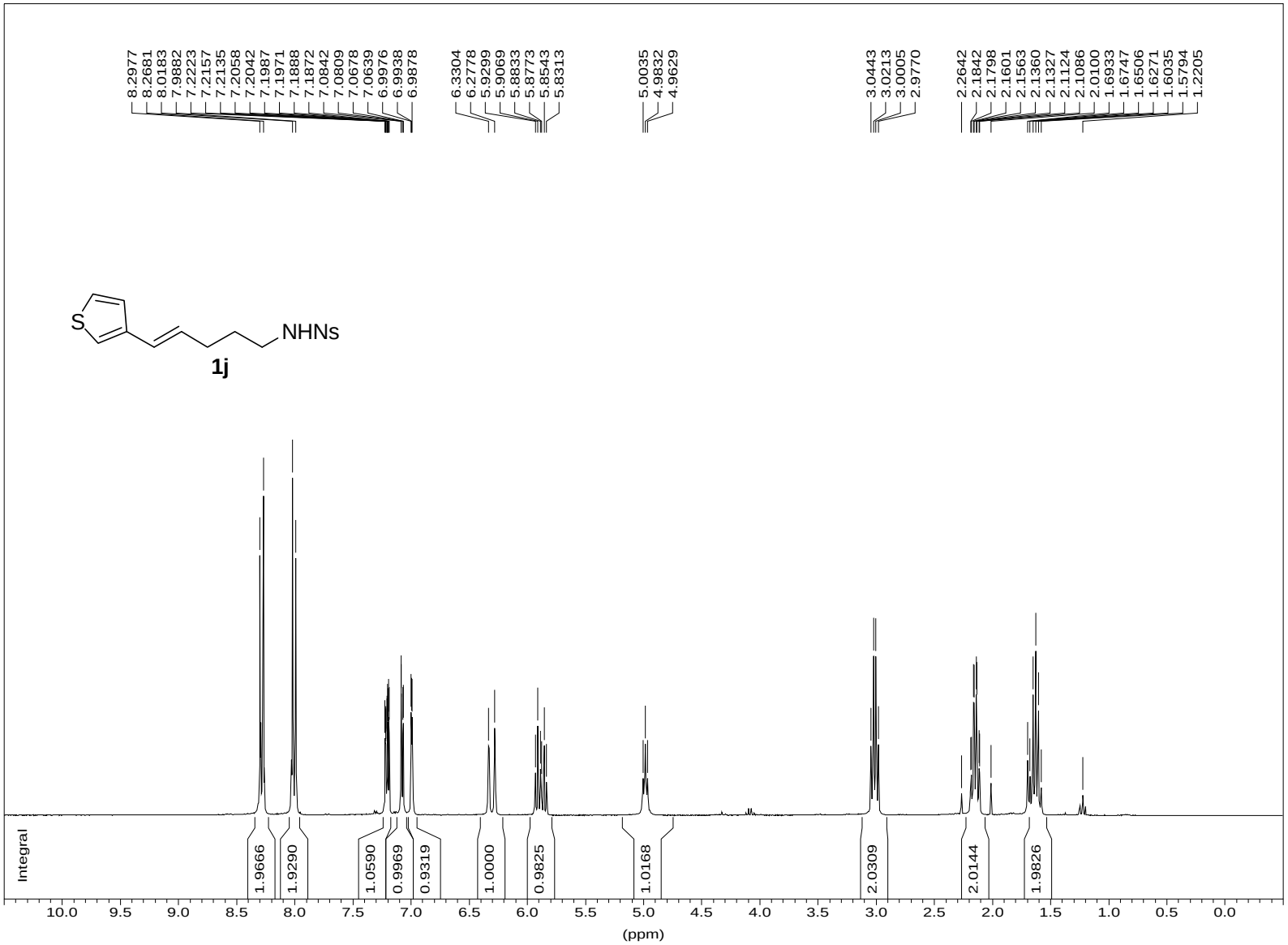
BF1	:	75.4677490 MH
LOCNUC	:	2H
NS	:	426
O1	:	7924.11 Hz
PULPROG	:	zgpg30
SFO1	:	75.4756731 MH
SOLVENT	:	Acetone
SW	:	238.2968 ppm

*** Processing Parameters ***

LB	:	1.00 Hz
PHC0	:	6.391 deg
PHC1	:	-0.586 deg

1H normal range AC300

3-th

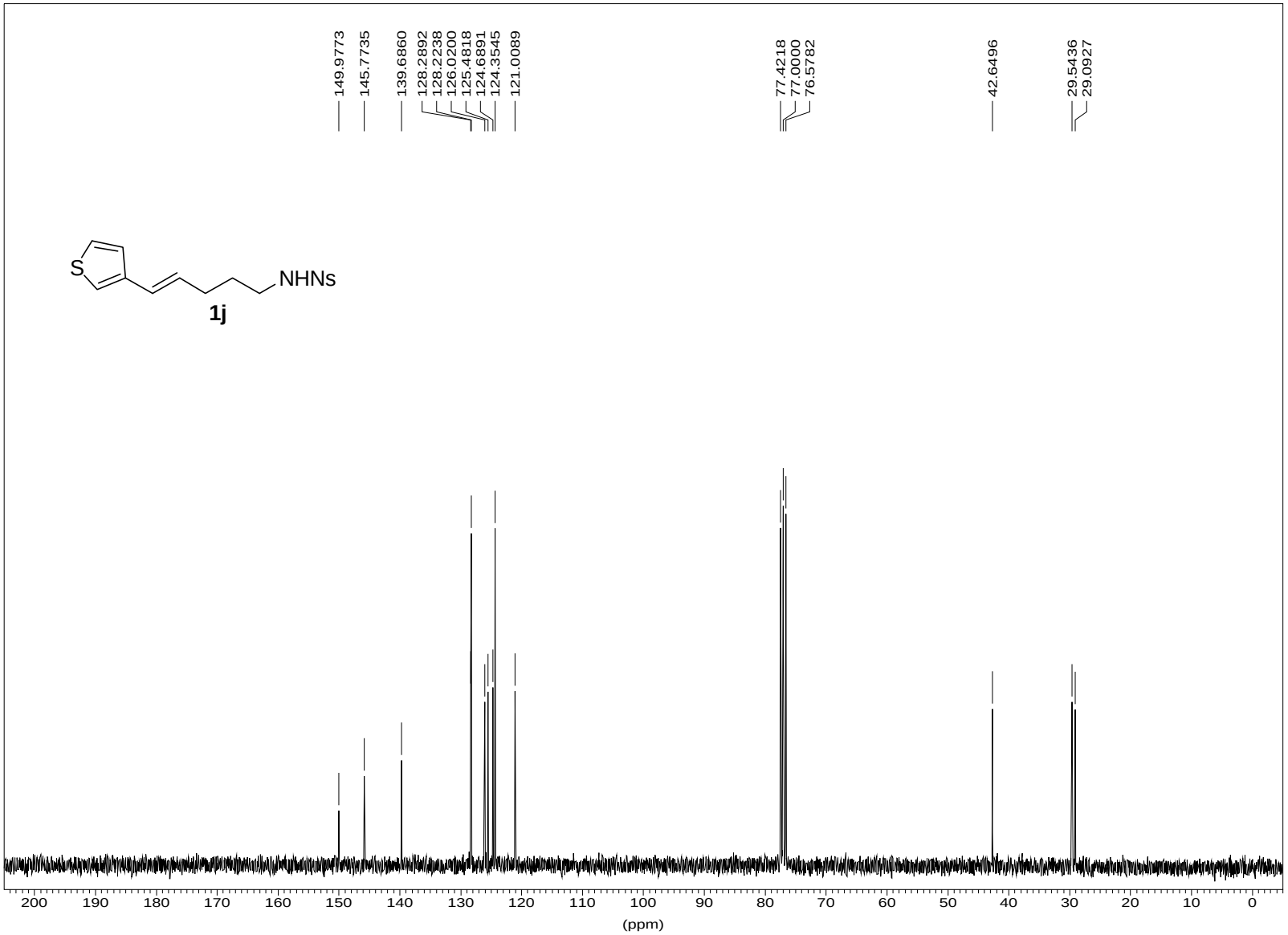


*** Current Data Parameters ***

NAME	:	se14zl
EXPNO	:	1
PROCNO	:	1
*** Acquisition Parameters ***		
BF1	:	300.1300000 MHz
LOCNUC	:	2H
NS	:	8
O1	:	1853.43 Hz
PULPROG	:	zg30
SFO1	:	300.1318534 MHz
SOLVENT	:	CDCl3
SW	:	17.9519 ppm
*** Processing Parameters ***		
LB	:	0.30 Hz
PHC0	:	20.975 degre
PHC1	:	-0.086 degre

13C Standard AC300

3-th



*** Current Data Parameters ***

NAME	:	se14zl
EXPNO	:	2
PROCNO	:	1

*** Acquisition Parameters ***

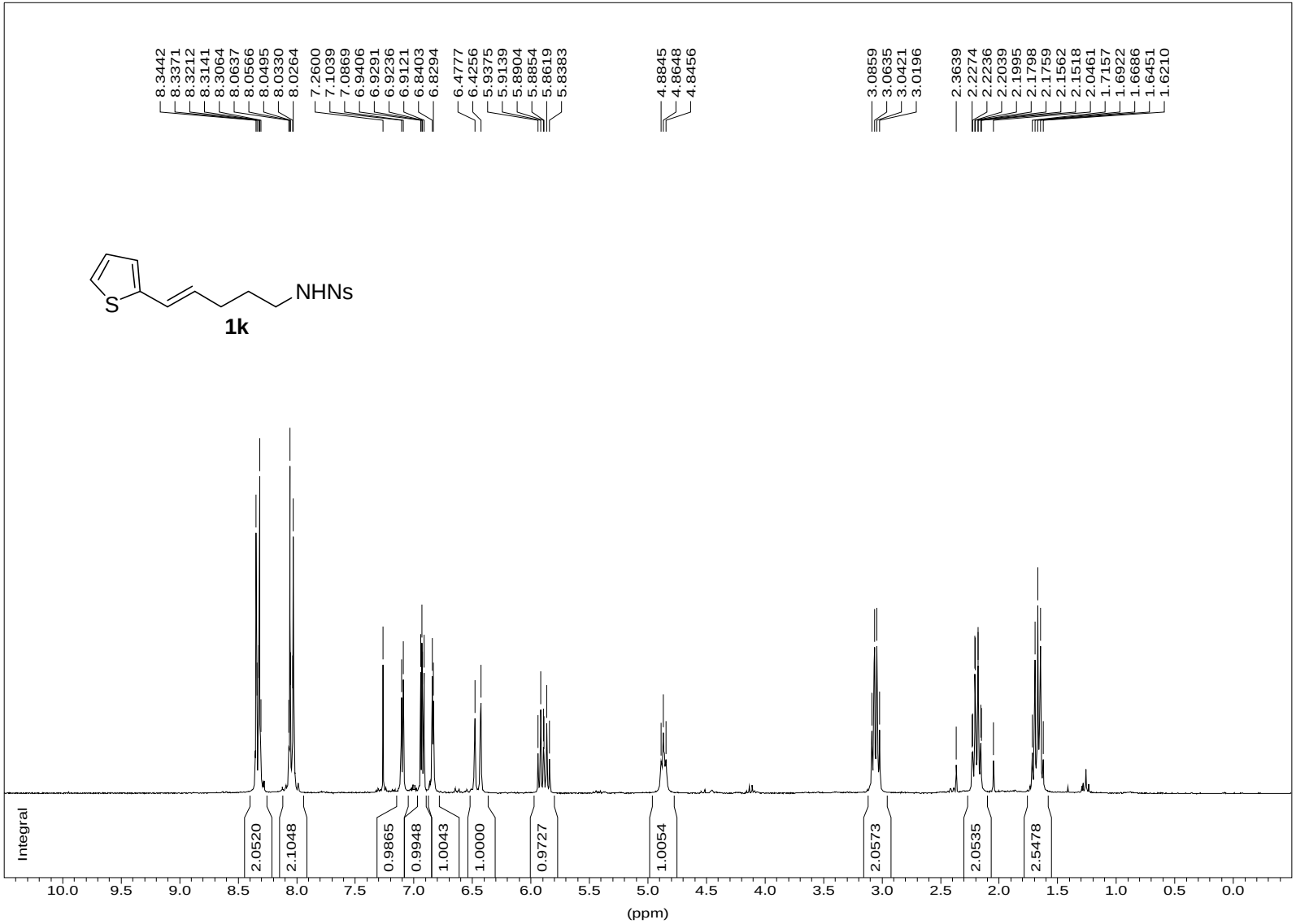
BF1	:	75.4677490 MH
LOCNUC	:	2H
NS	:	426
O1	:	7924.11 Hz
PULPROG	:	zgpg30
SFO1	:	75.4756731 MH
SOLVENT	:	CDCl3
SW	:	238.2968 ppn

*** Processing Parameters ***

LB	:	1.00 Hz
PHC0	:	11.970 deg
PHC1	:	-10.221 deg

1H normal range AC300

2-th

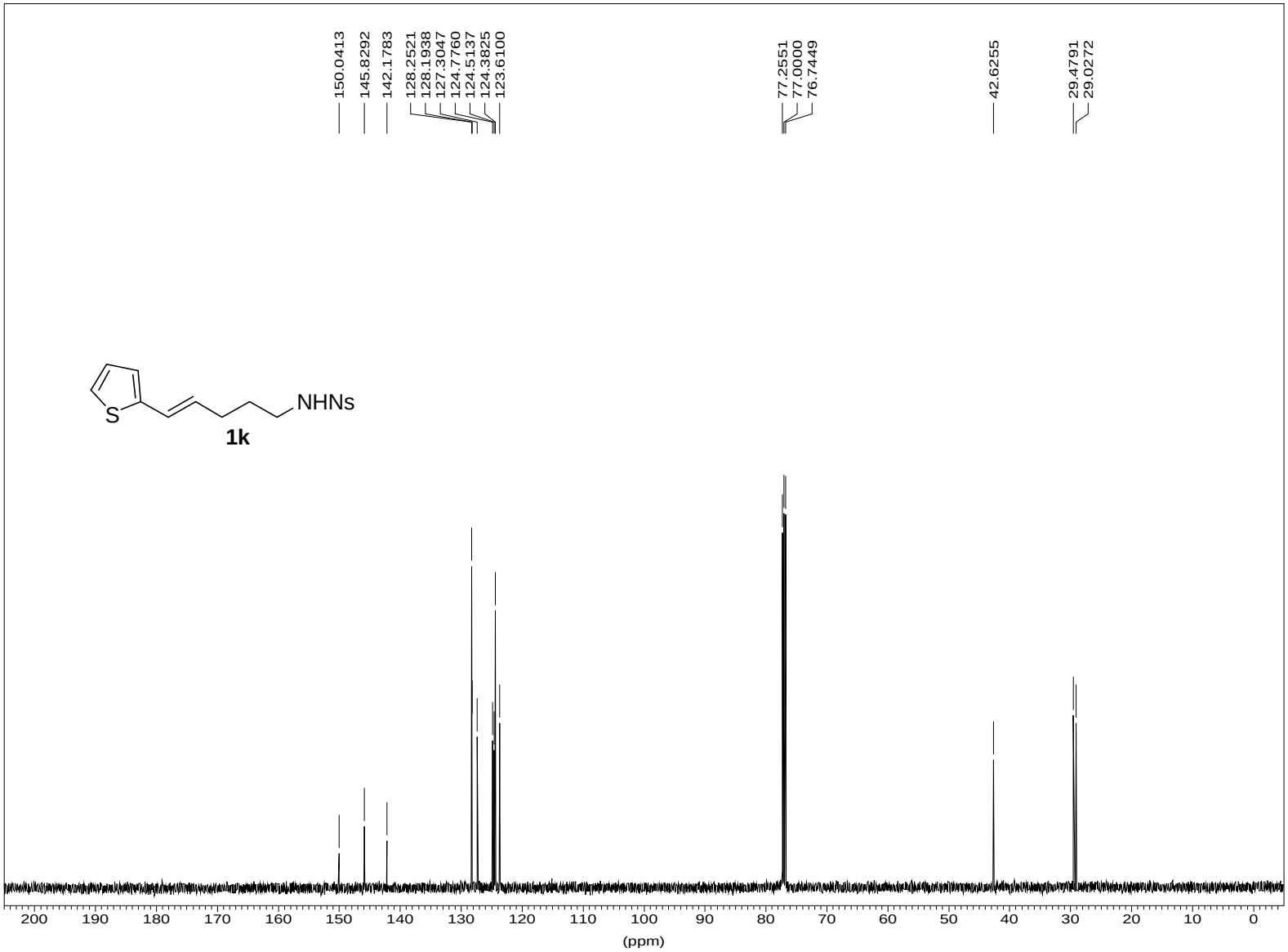


*** Current Data Parameters ***

NAME	:	se14zl
EXPNO	:	3
PROCNO	:	1
*** Acquisition Parameters ***		
BF1	:	300.1300000 MHz
LOCNUC	:	2H
NS	:	8
O1	:	1853.43 Hz
PULPROG	:	zg30
SFO1	:	300.1318534 MHz
SOLVENT	:	CDCl3
SW	:	17.9519 ppm
*** Processing Parameters ***		
LB	:	0.30 Hz
PHC0	:	19.671 degr
PHC1	:	3.591 degr

13C AMX500

2-th



*** Current Data Parameters ***

NAME	:	zl0914
EXPNO	:	2
PROCNO	:	1

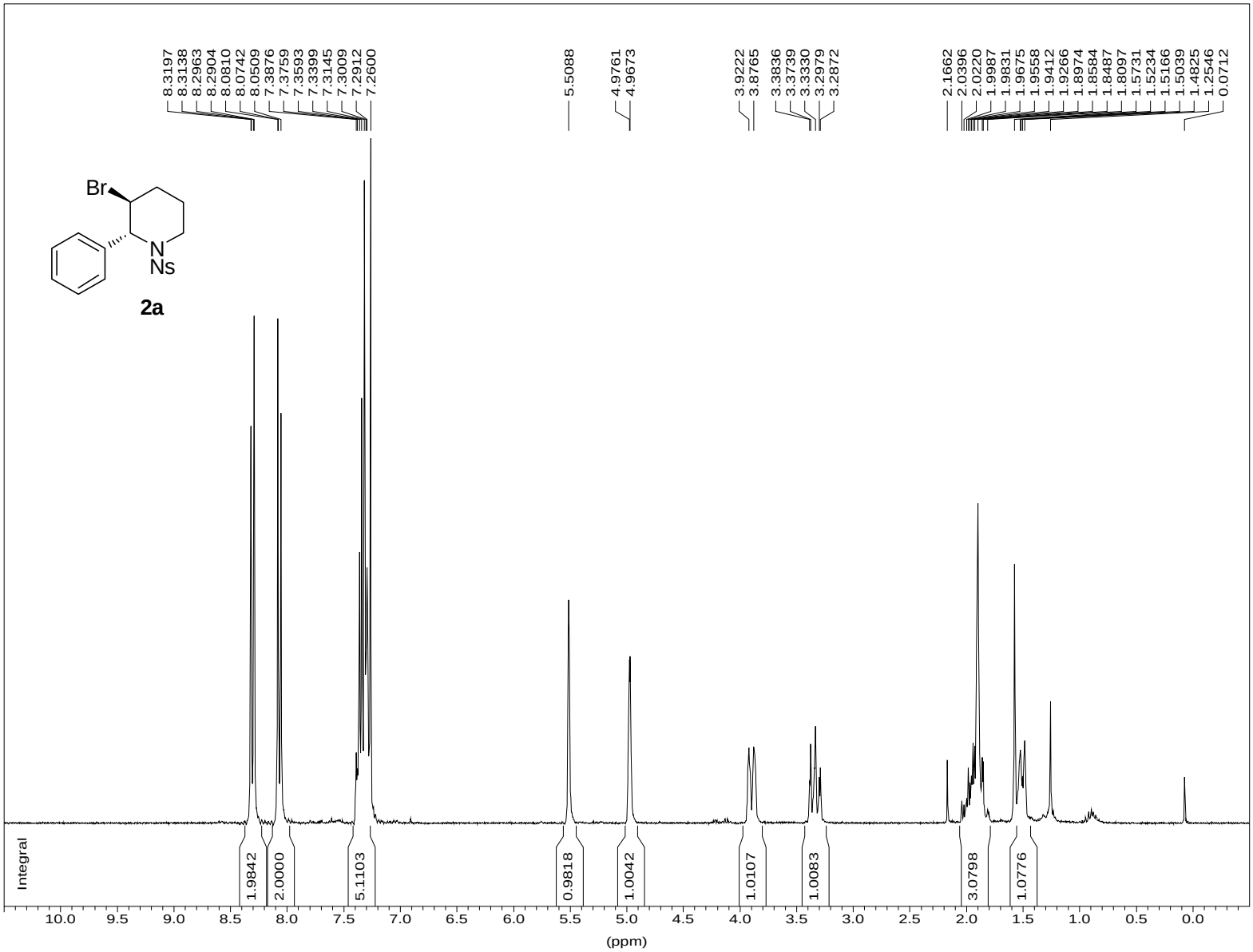
*** Acquisition Parameters ***

BF1	:	125.7577890 MHz
LOCNUC	:	2H
NS	:	176
O1	:	13204.57 Hz
PULPROG	:	zgpg30
SFO1	:	125.7709936 MHz
SOLVENT	:	CDCl3
SW	:	238.7675 ppm

*** Processing Parameters ***

LB	:	1.00 Hz
PHC0	:	306.994 degree
PHC1	:	21.928 degree

trans-prod-CDCl3



*** Current Data Parameters ***

NAME	:	ap09zl
EXPNO	:	6
PROCNO	:	1

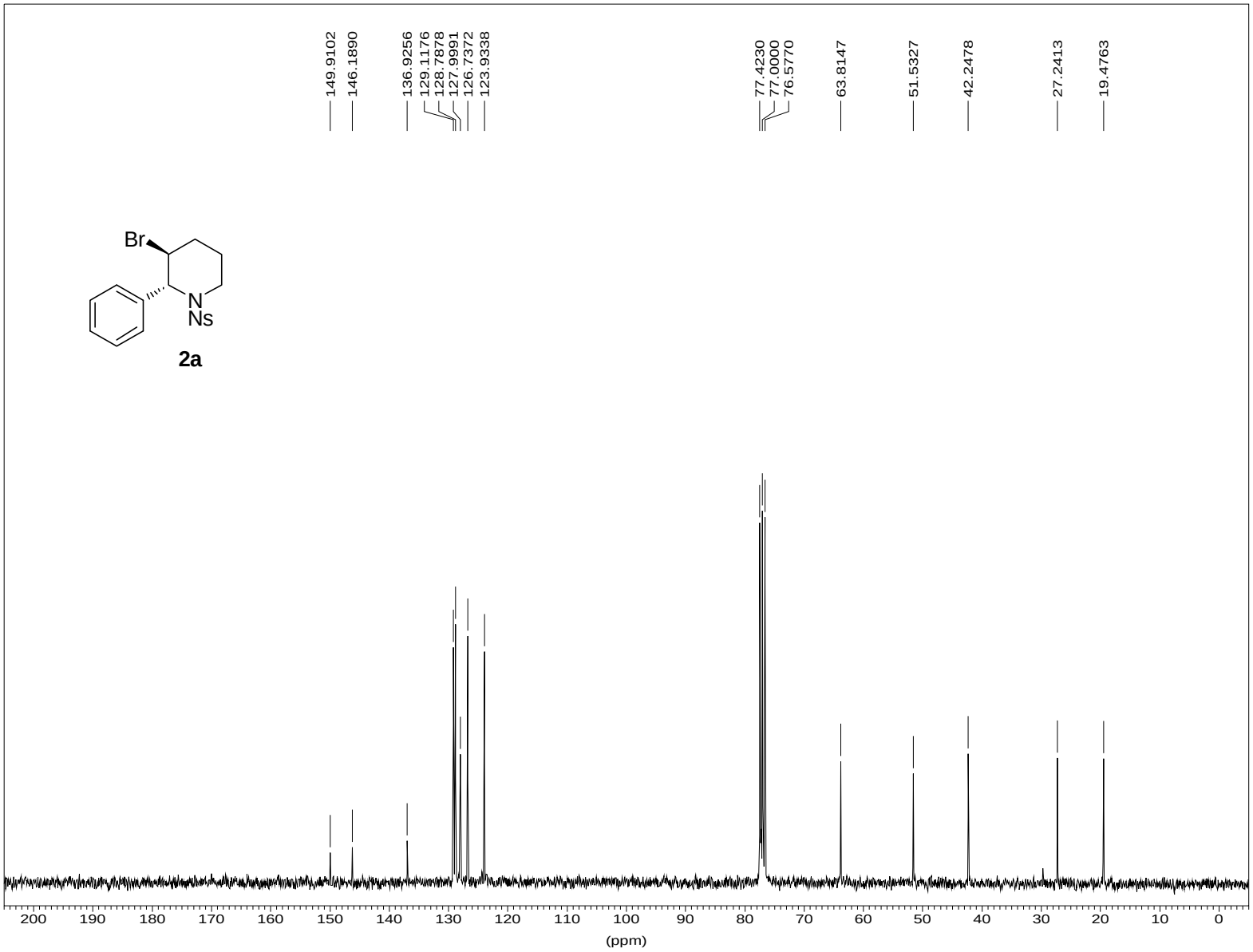
*** Acquisition Parameters ***

BF1	:	300.1300000 MHz
LOCNUC	:	2H
NS	:	8
O1	:	1250.00 Hz
PULPROG	:	zg30
SFO1	:	300.1312500 MHz
SOLVENT	:	CDCl3
SW	:	15.9573 ppm

*** Processing Parameters ***

LB	:	0.10 Hz
PHC0	:	467.449 degree
PHC1	:	5.547 degree

trans-prod-CDCl3



*** Current Data Parameters ***

NAME	:	ap09zl
EXPNO	:	7
PROCNO	:	1

*** Acquisition Parameters ***

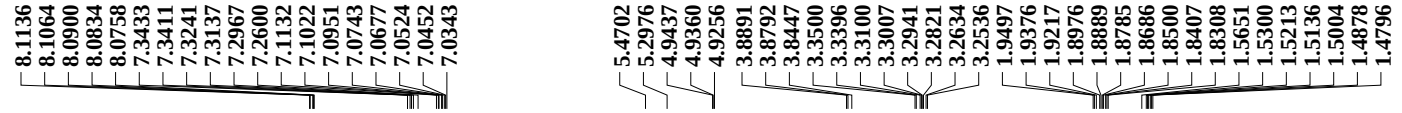
BF1	:	75.4677190 MHz
LOCNUC	:	2H
NS	:	282
O1	:	8301.45 Hz
PULPROG	:	zgdc
SFO1	:	75.4760204 MHz
SOLVENT	:	CDCl3
SW	:	234.9156 ppm

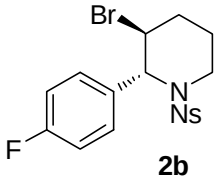
*** Processing Parameters ***

LB	:	3.00 Hz
PHC0	:	392.442 degree
PHC1	:	9.704 degree

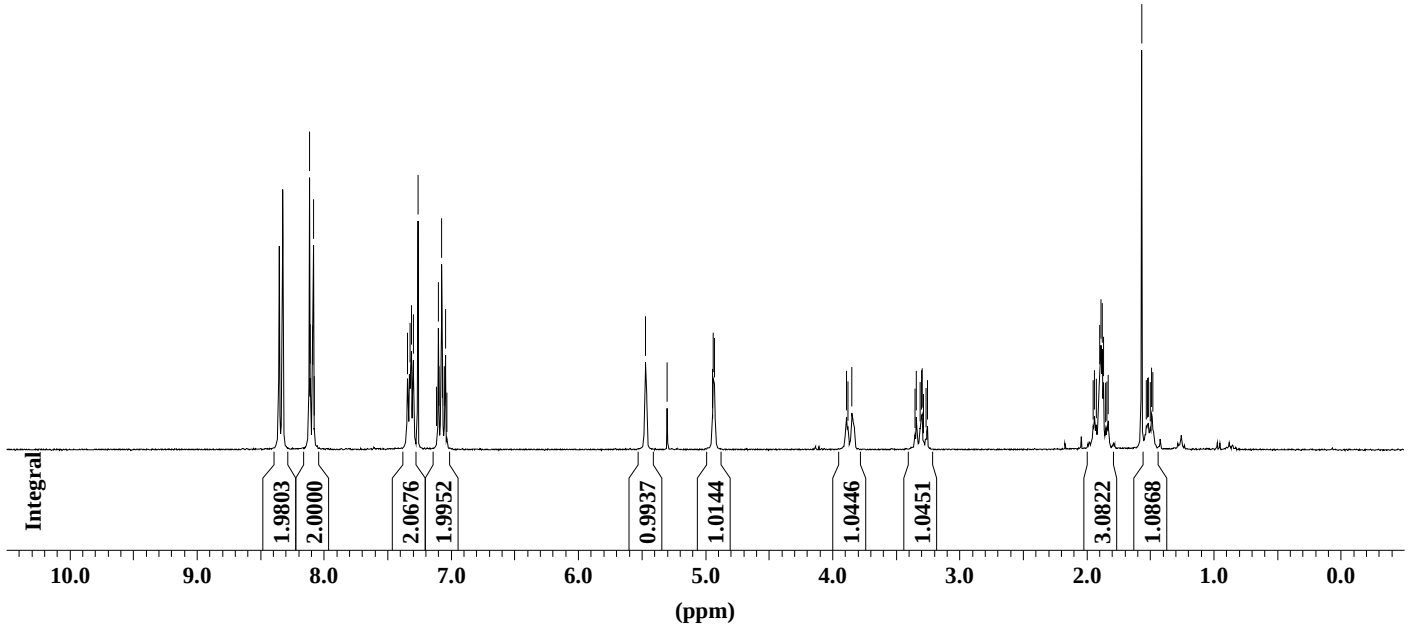
1H normal range AC300

3203-2





2b



***** Current Data Parameters *****

NAME	:	se16zl
EXPNO	:	3
PROCNO	:	1

***** Acquisition Parameters *****

LOCNUC	:	2H
NS	:	8
NUCLEUS	:	off
O1	:	1853.43 Hz
PULPROG	:	zg30
SFO1	:	300.1318534 MHz
SOLVENT	:	CDCl3
SW	:	17.9519 ppm
TD	:	32768
TE	:	297.4 K

***** Processing Parameters *****

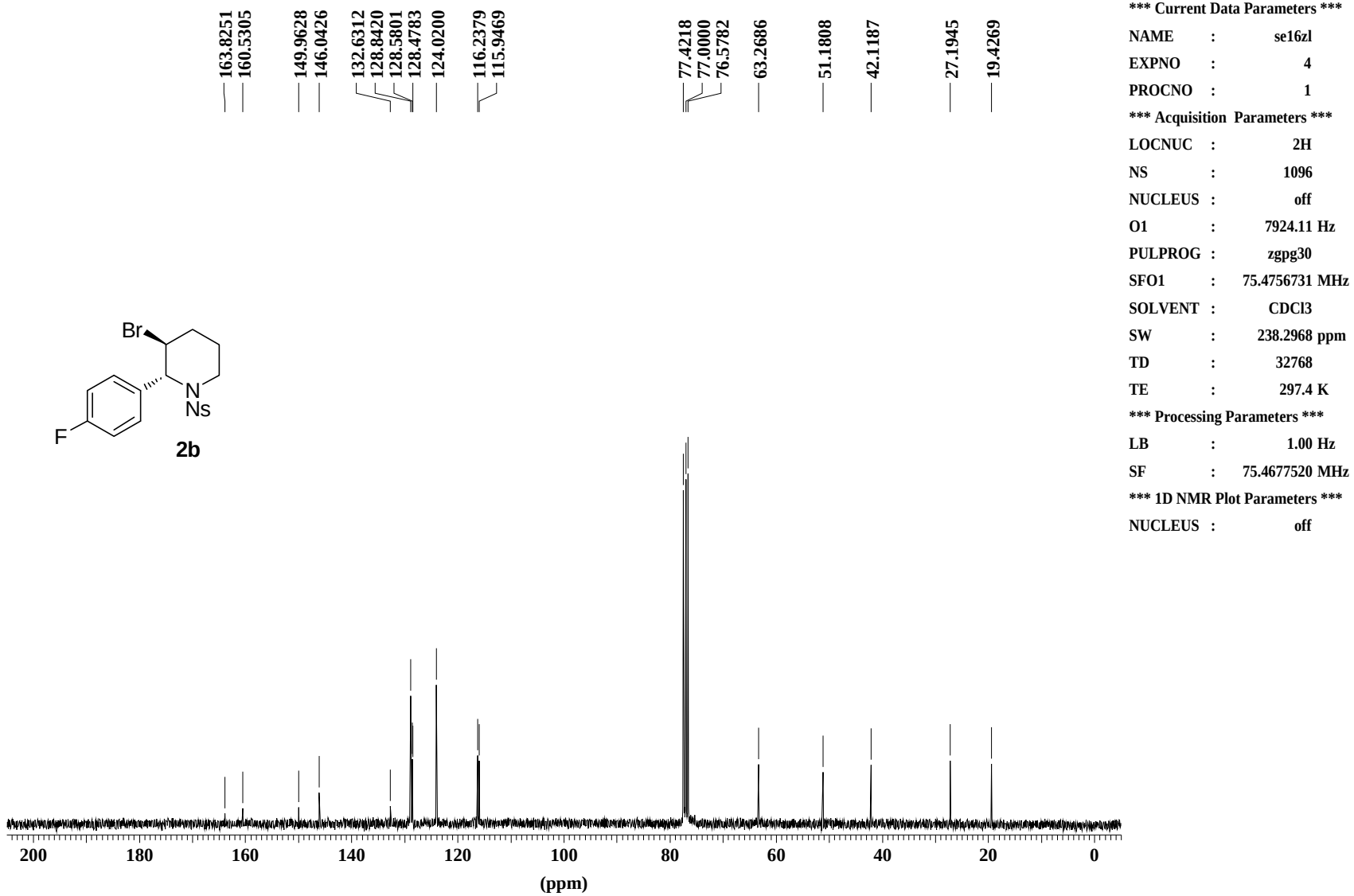
LB	:	0.30 Hz
SF	:	300.1300130 MHz

***** 1D NMR Plot Parameters *****

NUCLEUS	:	off

13C Standard AC300

3203-2



***** Current Data Parameters *****

NAME	:	se16zl
EXPNO	:	4
PROCNO	:	1

***** Acquisition Parameters *****

LOCNUC	:	2H
NS	:	1096
NUCLEUS	:	off
O1	:	7924.11 Hz
PULPROG	:	zgpg30
SFO1	:	75.4756731 MHz
SOLVENT	:	CDCl3
SW	:	238.2968 ppm
TD	:	32768
TE	:	297.4 K

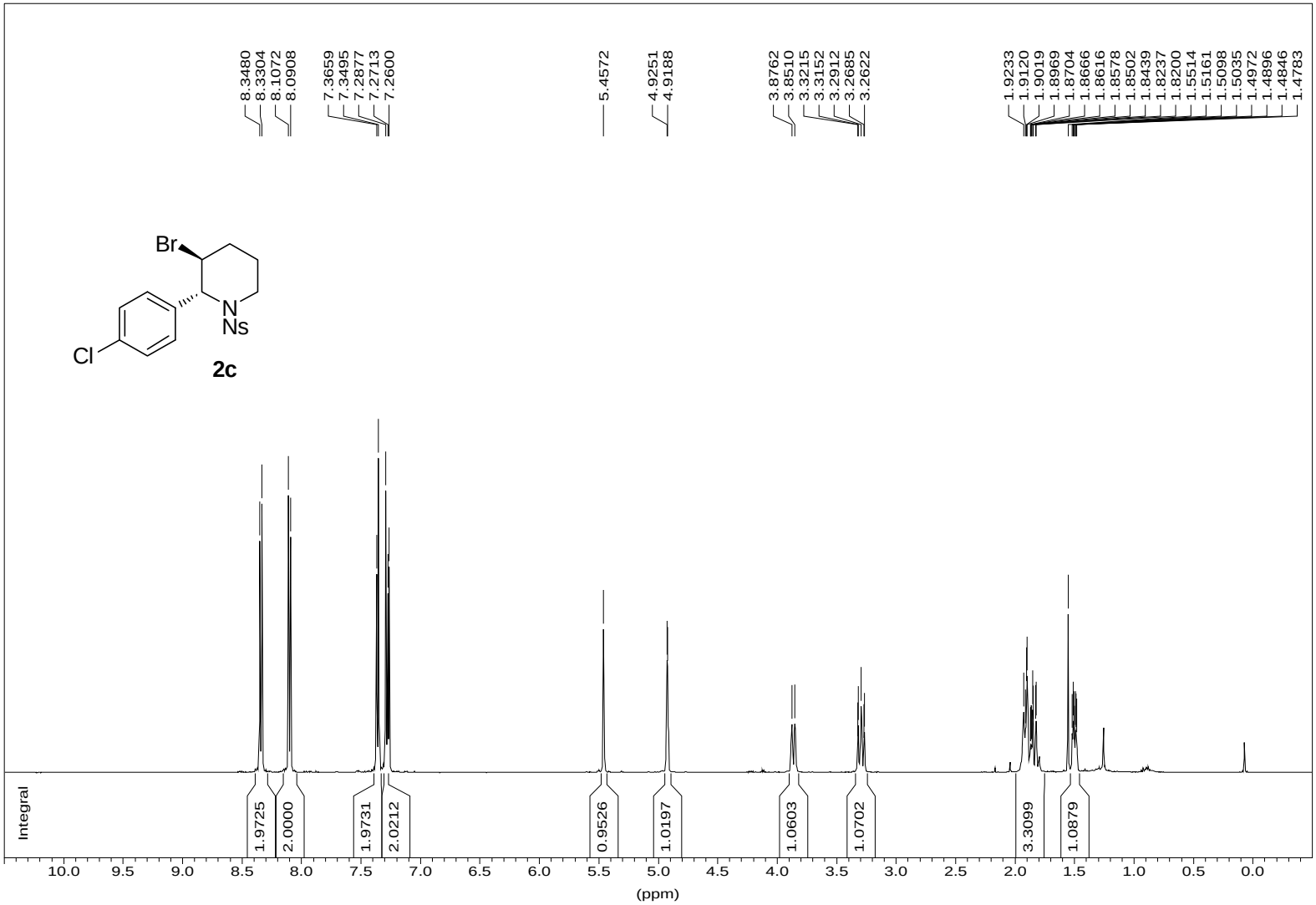
***** Processing Parameters *****

LB	:	1.00 Hz
SF	:	75.4677520 MHz

***** 1D NMR Plot Parameters *****

NUCLEUS	:	off

1H AMX500 zl 3203-1



*** Current Data Parameters ***

NAME	:	ck0824
EXPNO	:	5
PROCNO	:	1

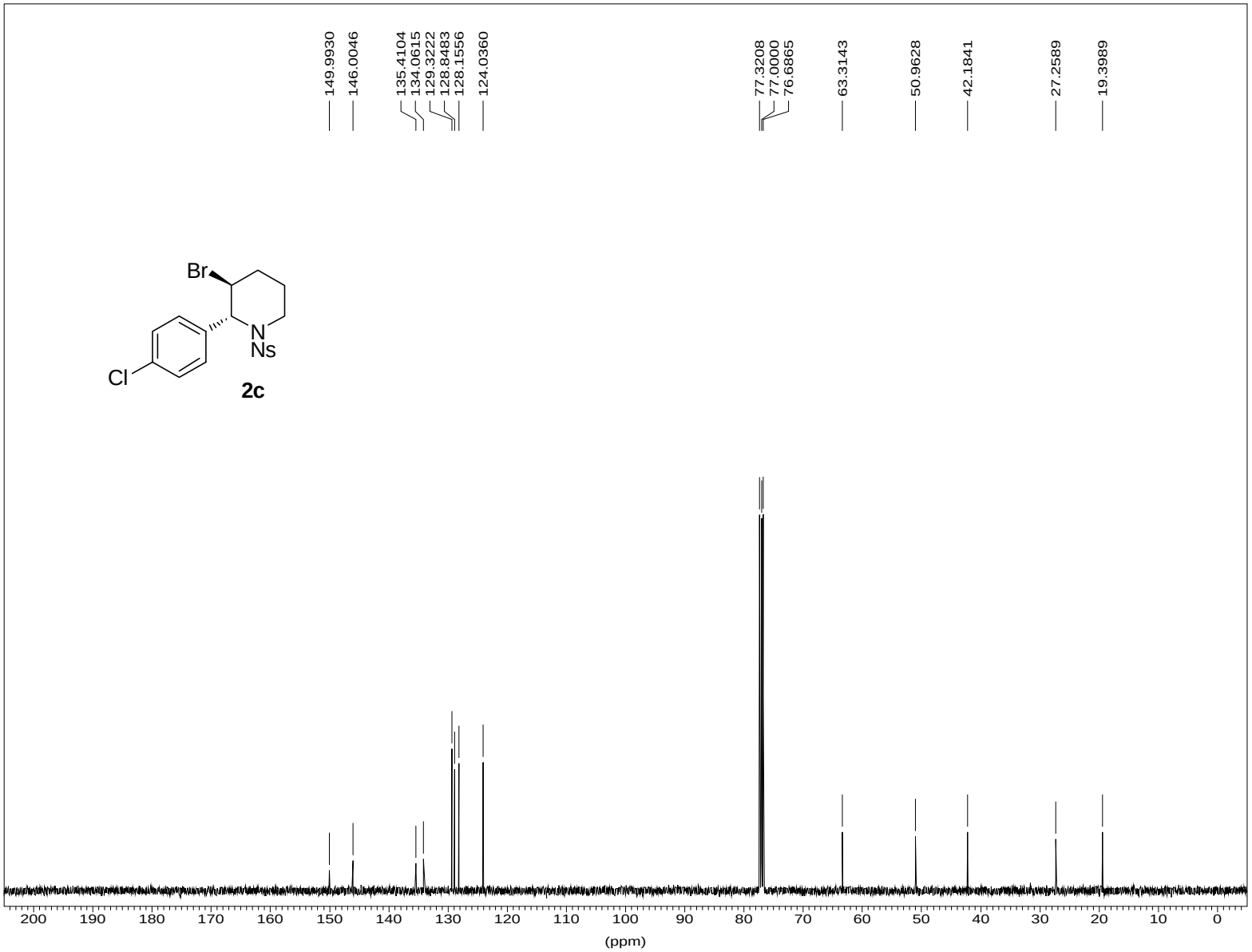
*** Acquisition Parameters ***

BF1	:	500.1300000 MHz
LOCNUC	:	2H
NS	:	8
O1	:	3088.51 Hz
PULPROG	:	zg30
SFO1	:	500.1330885 MHz
SOLVENT	:	CDCl3
SW	:	20.6557 ppm

*** Processing Parameters ***

LB	:	0.30 Hz
PHC0	:	282.393 degree
PHC1	:	2.046 degree

3203-1



*** Current Data Parameters ***

NAME	:	aug23zl
EXPNO	:	4
PROCNO	:	1

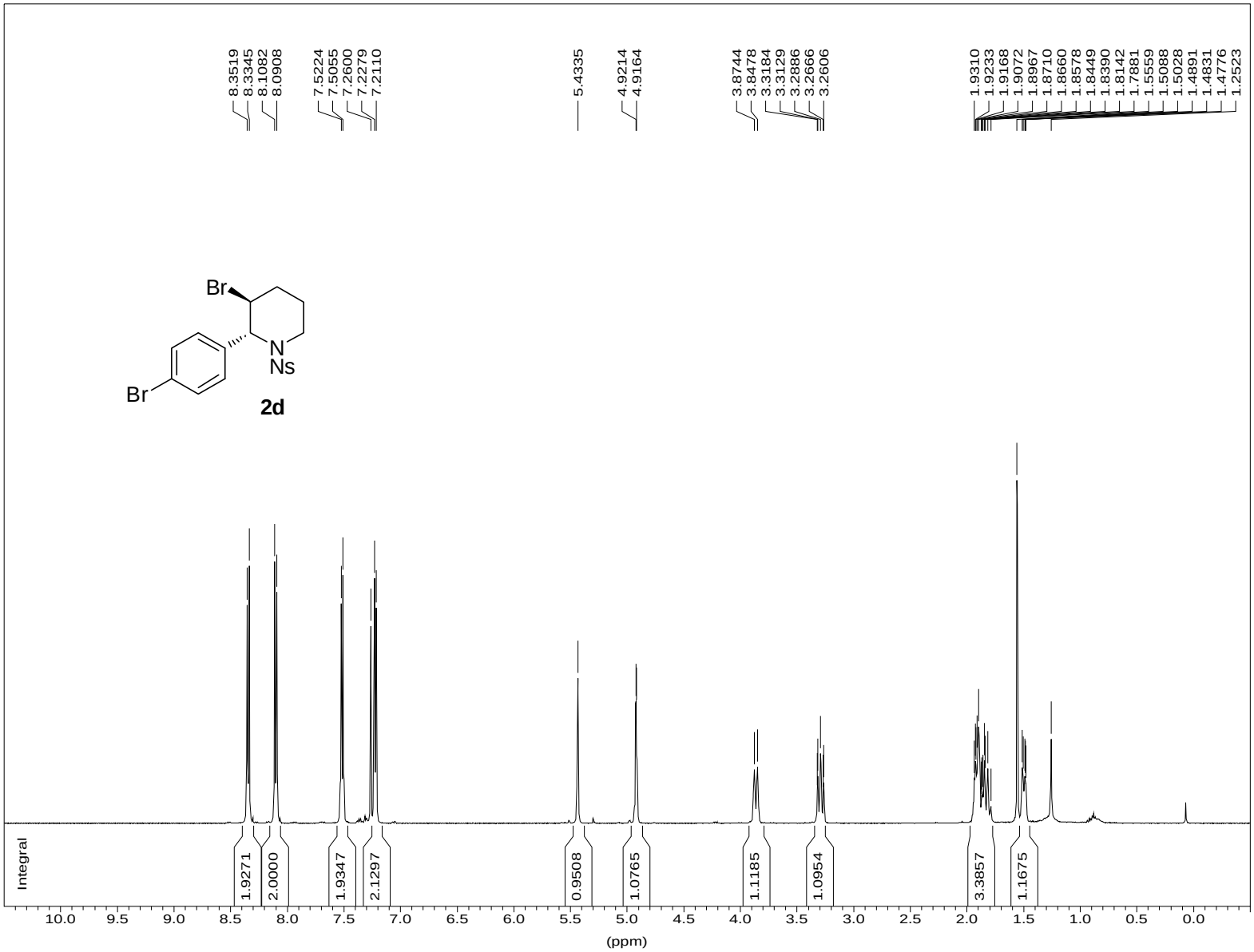
*** Acquisition Parameters ***

BF1	:	100.6127690 MHz
LOCNUC	:	2H
NS	:	225
O1	:	11067.40 Hz
PULPROG	:	zgpg30
SFO1	:	100.6238364 MHz
SOLVENT	:	CDCl3
SW	:	238.8943 ppm

*** Processing Parameters ***

LB	:	1.00 Hz
PHC0	:	106.346 degree
PHC1	:	-77.397 degree

4Br-P



*** Current Data Parameters ***

NAME	:	zl1209
EXPNO	:	4
PROCNO	:	1

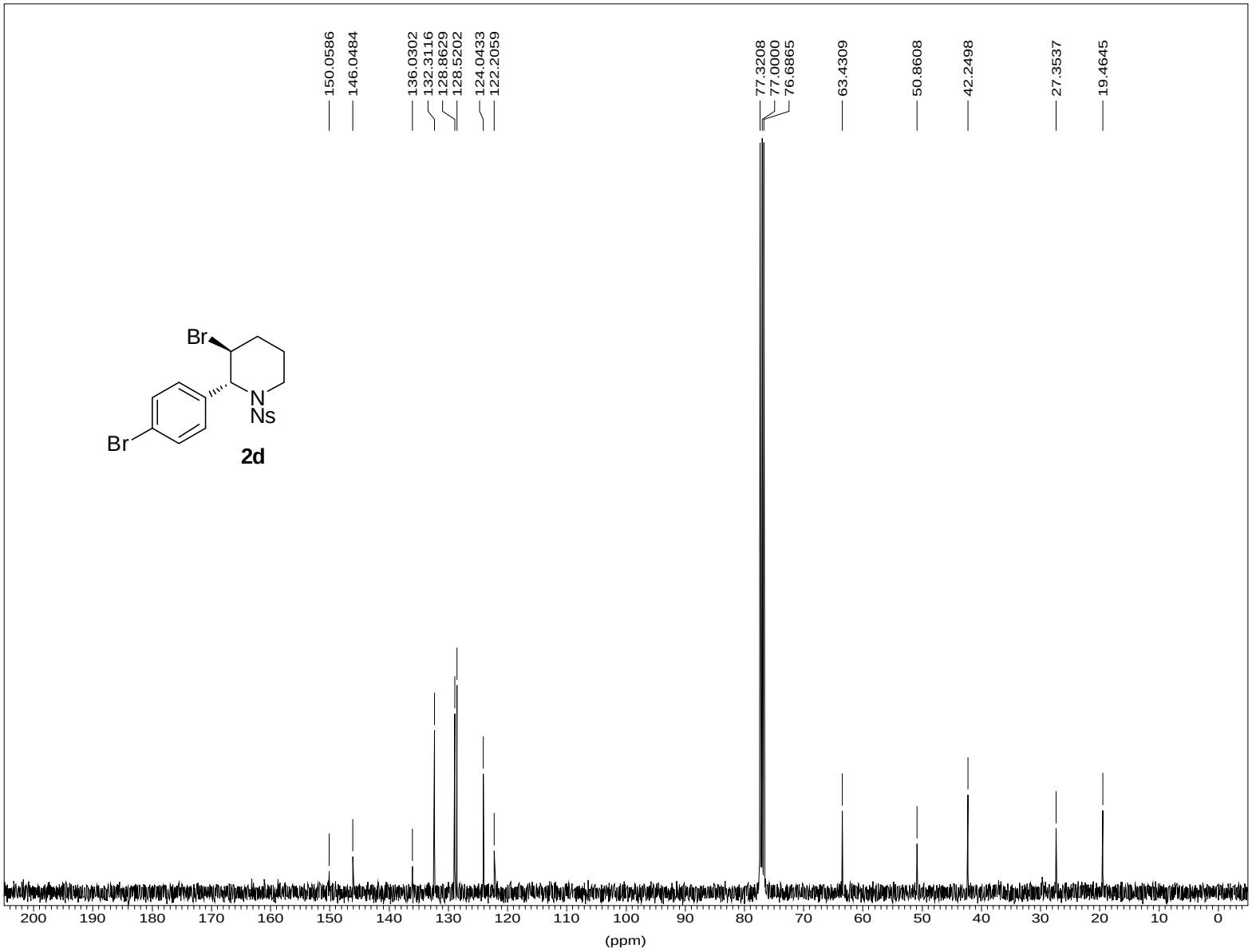
*** Acquisition Parameters ***

BF1	:	500.2300000 MHz
LOCNUC	:	2H
NS	:	8
O1	:	2751.27 Hz
PULPROG	:	zg
SFO1	:	500.2327513 MHz
SOLVENT	:	CDCl3
SW	:	15.0080 ppm

*** Processing Parameters ***

LB	:	0.10 Hz
PHC0	:	497.749 degree
PHC1	:	-5.478 degree

4Br-P



*** Current Data Parameters ***

NAME	:	dec09zl
EXPNO	:	2
PROCNO	:	1

*** Acquisition Parameters ***

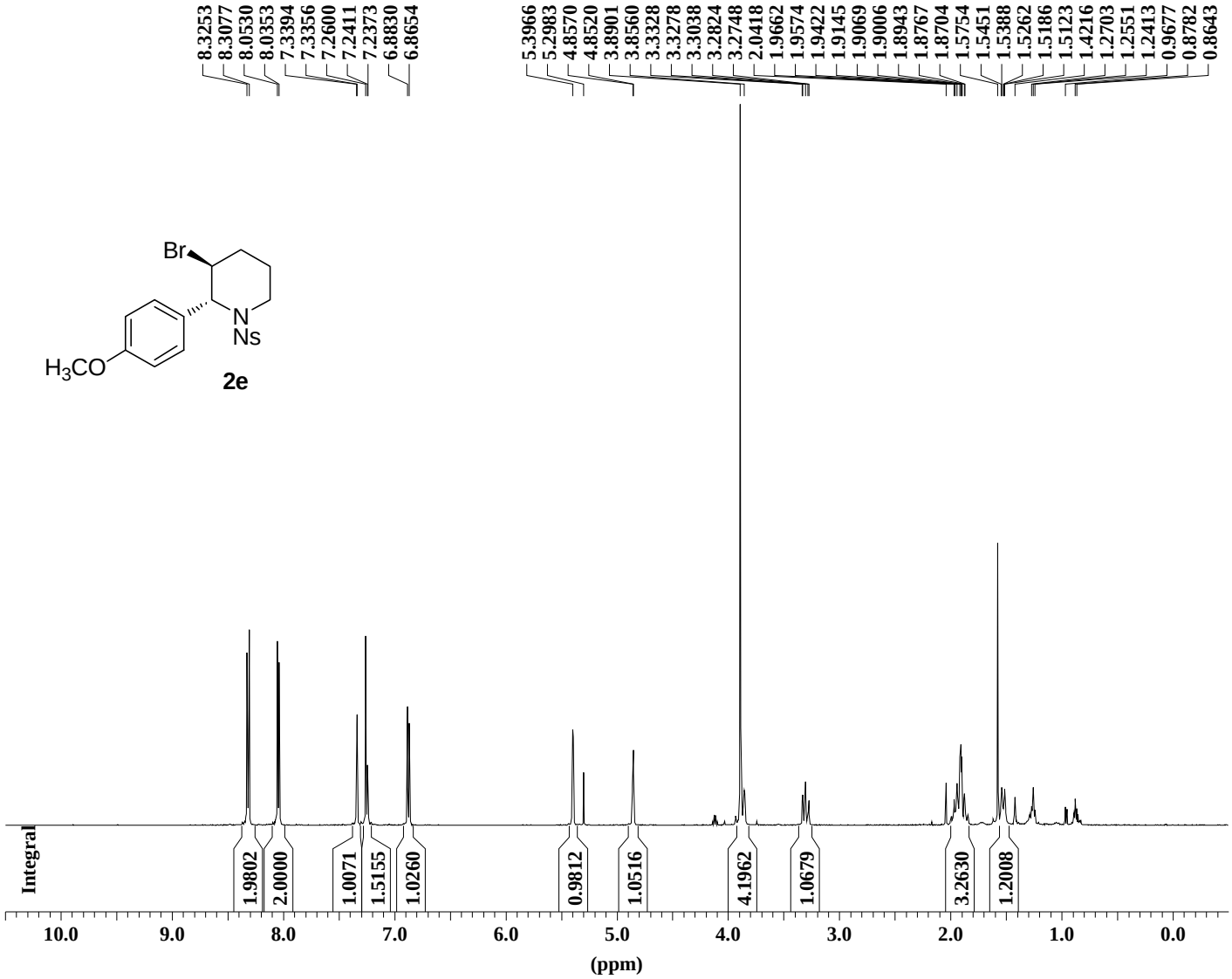
BF1	:	100.6127690 MHz
LOCNUC	:	2H
NS	:	1024
O1	:	11067.40 Hz
PULPROG	:	zgpg30
SFO1	:	100.6238364 MHz
SOLVENT	:	CDCl3
SW	:	238.8943 ppm

*** Processing Parameters ***

LB	:	1.00 Hz
PHC0	:	115.611 degree
PHC1	:	-62.139 degree

1H AMX500

3203-4



***** Current Data Parameters *****

NAME	:	zl0916
EXPNO	:	1
PROCNO	:	1

***** Acquisition Parameters *****

LOCNUC	:	2H
NS	:	8
NUCLEUS	:	off
O1	:	3088.51 Hz
PULPROG	:	zg30
SFO1	:	500.1330885 MHz
SOLVENT	:	CDCl3
SW	:	20.6557 ppm
TD	:	32768
TE	:	295.7 K

***** Processing Parameters *****

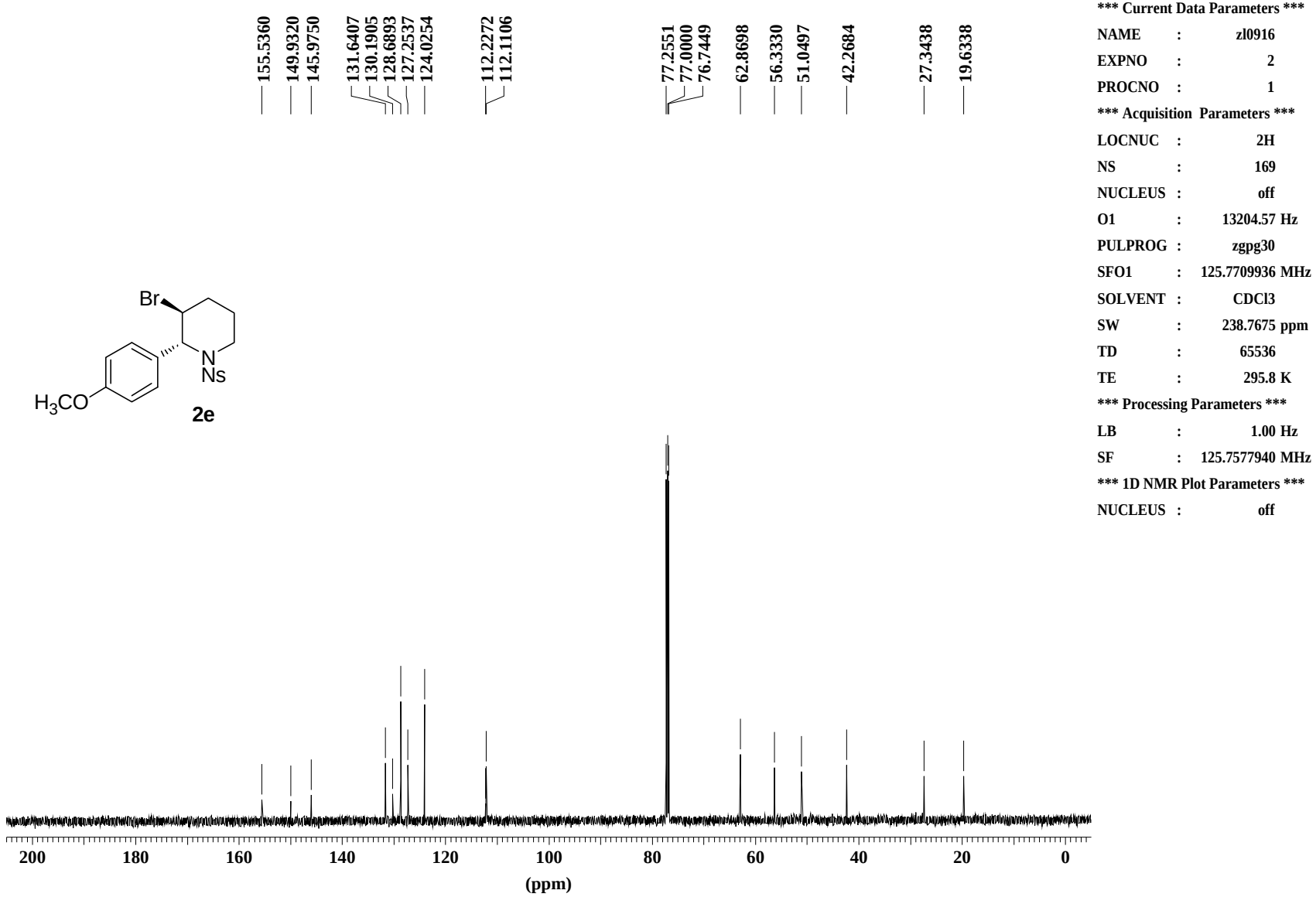
LB	:	0.30 Hz
SF	:	500.1300140 MHz

***** 1D NMR Plot Parameters *****

NUCLEUS	:	off

13C AMX500

3203-4



***** Current Data Parameters *****

NAME	:	zl0916
EXPNO	:	2
PROCNO	:	1

***** Acquisition Parameters *****

LOCNUC	:	2H
NS	:	169
NUCLEUS	:	off
O1	:	13204.57 Hz
PULPROG	:	zgpg30
SFO1	:	125.7709936 MHz
SOLVENT	:	CDCl3
SW	:	238.7675 ppm
TD	:	65536
TE	:	295.8 K

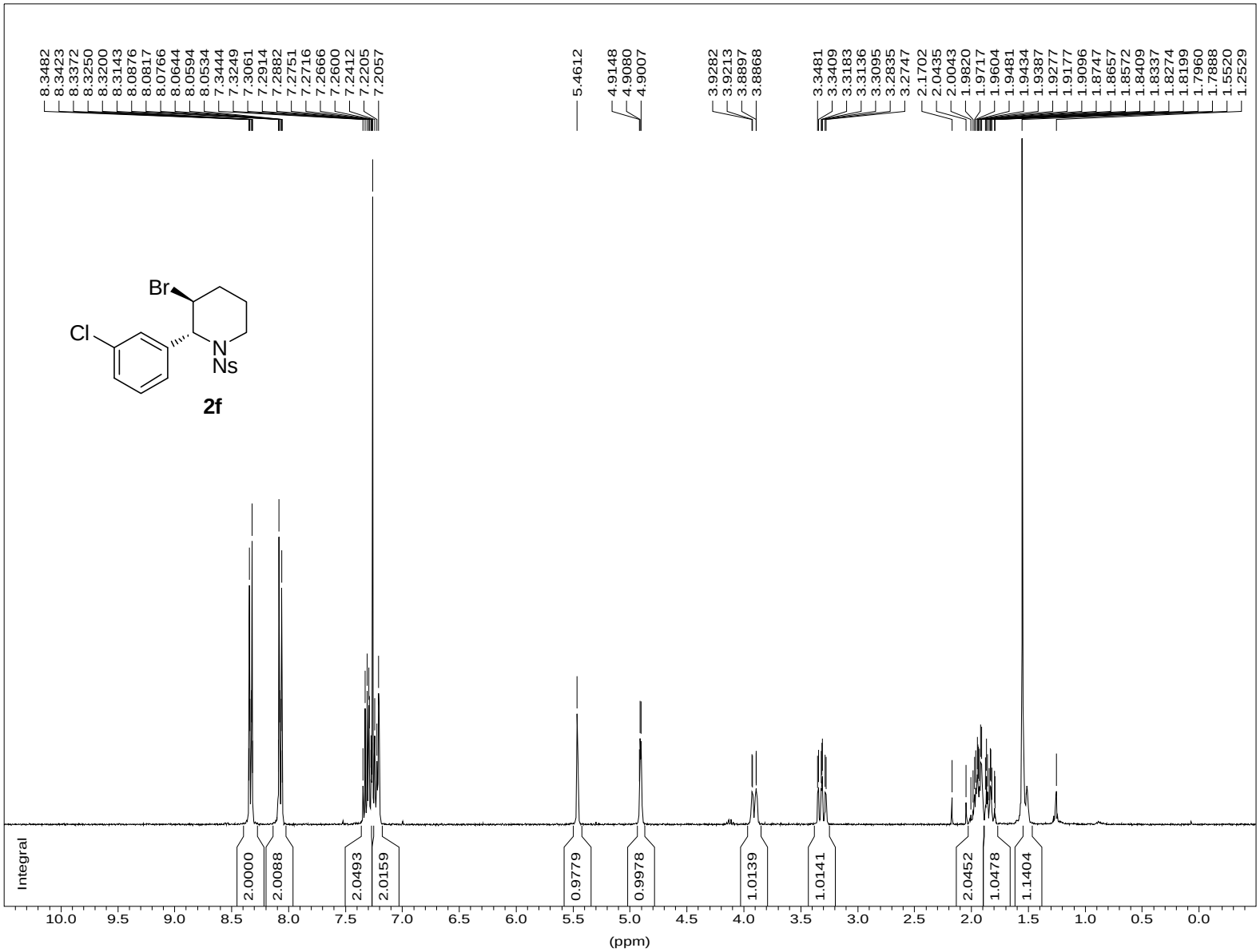
***** Processing Parameters *****

LB	:	1.00 Hz
SF	:	125.7577940 MHz

***** 1D NMR Plot Parameters *****

NUCLEUS	:	off

3Cl



*** Current Data Parameters ***

NAME	:	dec03zl
EXPNO	:	1
PROCNO	:	1

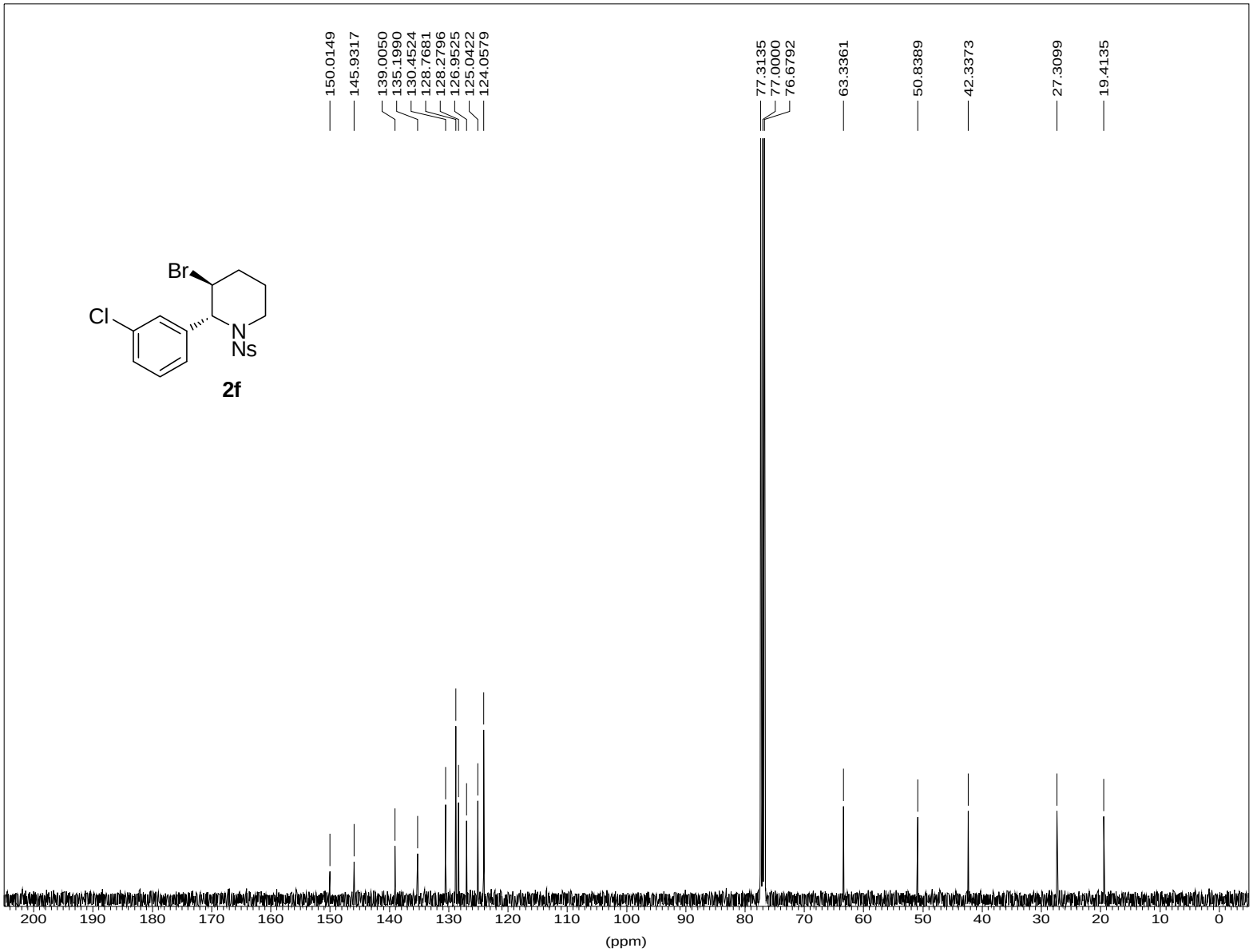
*** Acquisition Parameters ***

BF1	:	400.1300000 MHz
LOCNUC	:	2H
NS	:	8
O1	:	2470.97 Hz
PULPROG	:	zg30
SFO1	:	400.1324710 MHz
SOLVENT	:	CDCl3
SW	:	20.5524 ppm

*** Processing Parameters ***

LB	:	0.30 Hz
PHC0	:	-47.510 degree
PHC1	:	-18.713 degree

3Cl



*** Current Data Parameters ***

NAME	:	dec03zl
EXPNO	:	2
PROCNO	:	1

*** Acquisition Parameters ***

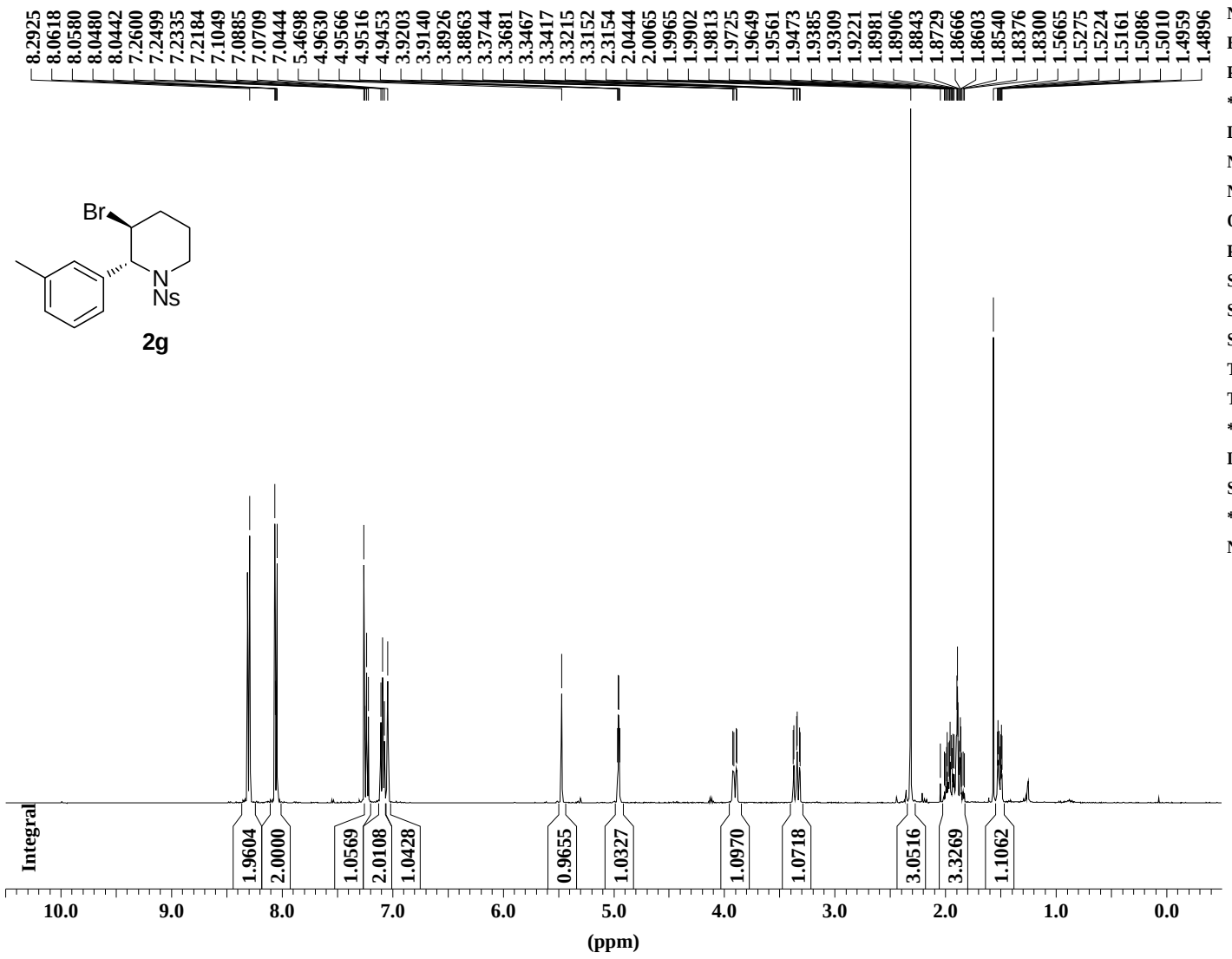
BF1	:	100.6127690 MHz
LOCNUC	:	2H
NS	:	1024
O1	:	11067.40 Hz
PULPROG	:	zgpg30
SFO1	:	100.6238364 MHz
SOLVENT	:	CDCl3
SW	:	238.8943 ppm

*** Processing Parameters ***

LB	:	1.00 Hz
PHC0	:	84.883 degree
PHC1	:	-33.166 degree

1H AMX500

3203-3



***** Current Data Parameters *****

NAME	:	zl0916
EXPNO	:	3
PROCNO	:	1

***** Acquisition Parameters *****

LOCNUC	:	2H
NS	:	8
NUCLEUS	:	off
O1	:	3088.51 Hz
PULPROG	:	zg30
SFO1	:	500.1330885 MHz
SOLVENT	:	CDCl3
SW	:	20.6557 ppm
TD	:	32768
TE	:	296.0 K

***** Processing Parameters *****

LB	:	0.30 Hz
SF	:	500.1300140 MHz

***** 1D NMR Plot Parameters *****

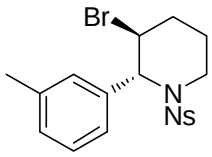
NUCLEUS	:	off

13C AMX500

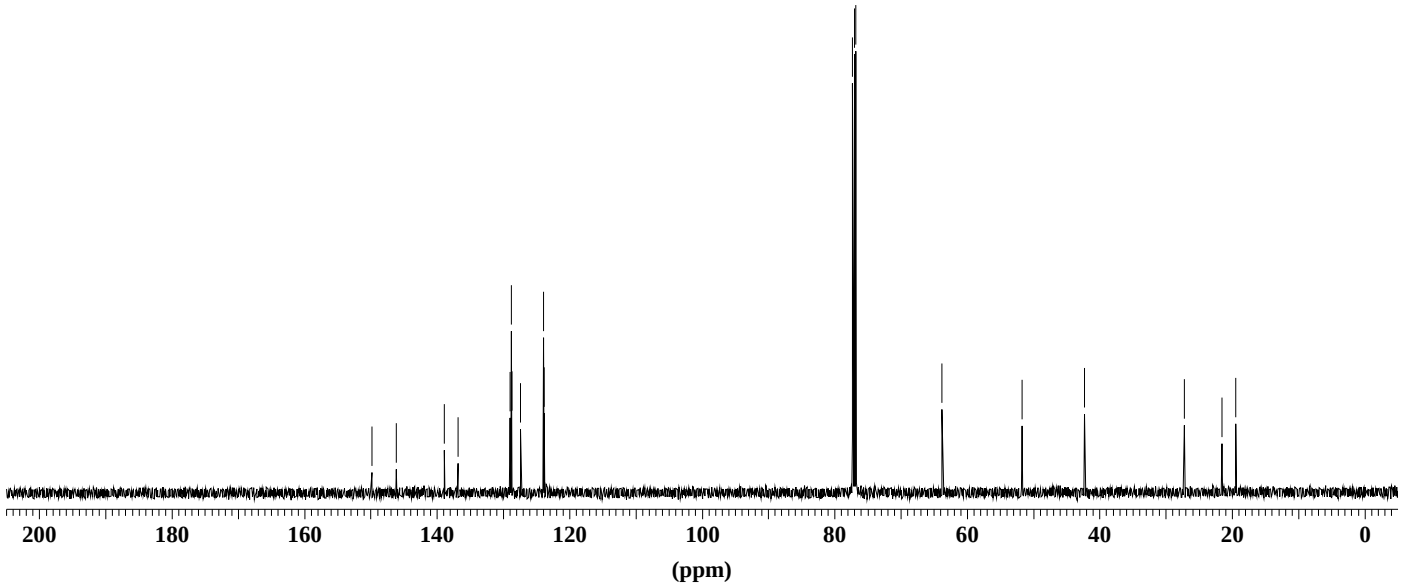
3203-3

149.8300
146.1717
138.8552
136.8147
128.9881
128.7549
128.7112
127.3703
123.9088
123.7703

77.2551
77.0000
76.7449
63.7588
51.7420
42.2975
27.1908
21.5722
19.4589



2g



*** Current Data Parameters ***

NAME : zl0916

EXPNO : 4

PROCNO : 1

*** Acquisition Parameters ***

LOCNUC : 2H

NS : 208

NUCLEUS : off

O1 : 13204.57 Hz

PULPROG : zgpg30

SFO1 : 125.7709936 MHz

SOLVENT : CDCl3

SW : 238.7675 ppm

TD : 65536

TE : 296.2 K

*** Processing Parameters ***

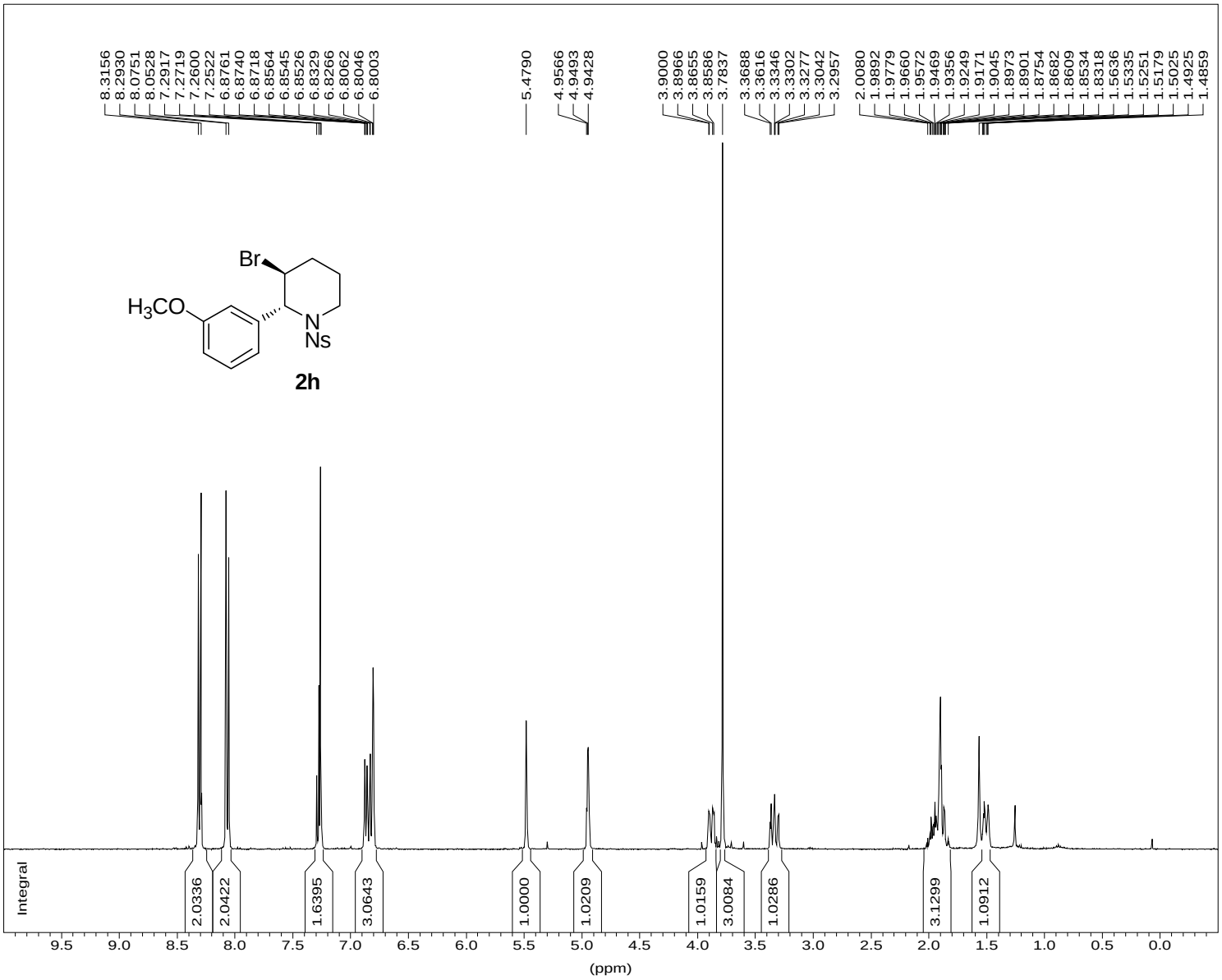
LB : 1.00 Hz

SF : 125.7577940 MHz

*** 1D NMR Plot Parameters ***

NUCLEUS : off

3OMe-P



*** Current Data Parameters ***

NAME	:	nov21zl
EXPNO	:	2
PROCNO	:	1

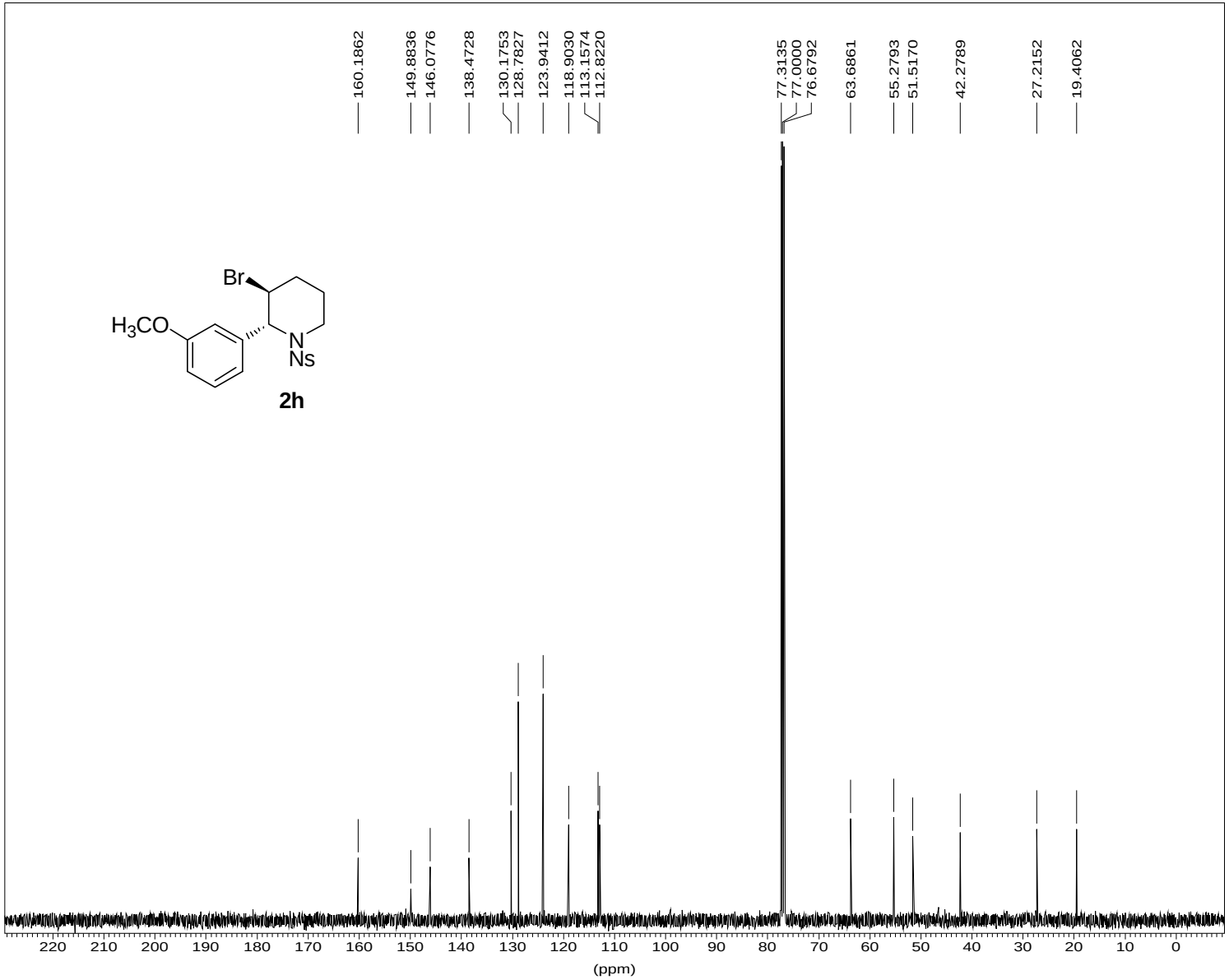
*** Acquisition Parameters ***

BF1	:	400.1300000 MHz
LOCNUC	:	2H
NS	:	8
O1	:	2470.97 Hz
PULPROG	:	zg30
SFO1	:	400.1324710 MHz
SOLVENT	:	CDCl3
SW	:	20.5524 ppm

*** Processing Parameters ***

LB	:	0.30 Hz
PHC0	:	-51.835 degree
PHC1	:	-15.073 degree

3OMe-P



*** Current Data Parameters ***

NAME	:	nov21zl
EXPNO	:	3
PROCNO	:	1

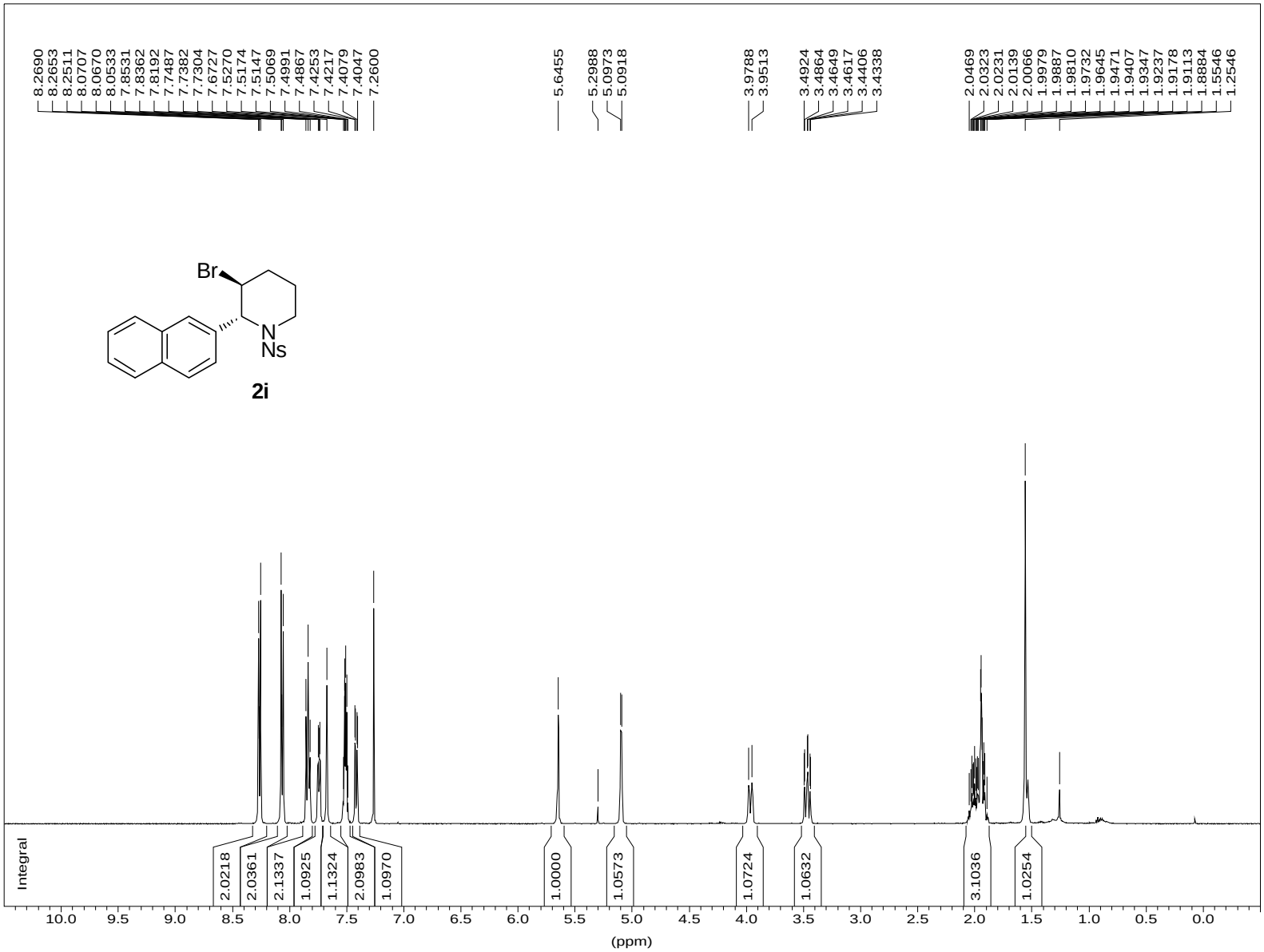
*** Acquisition Parameters ***

BF1	:	100.6127690 MHz
LOCNUC	:	2H
NS	:	325
O1	:	11067.40 Hz
PULPROG	:	zgpg30
SFO1	:	100.6238364 MHz
SOLVENT	:	CDCl3
SW	:	238.8943 ppm

*** Processing Parameters ***

LB	:	1.00 Hz
PHC0	:	91.395 degree
PHC1	:	-50.951 degree

2-naph-P



*** Current Data Parameters ***

NAME	:	zl1209
EXPNO	:	3
PROCNO	:	1

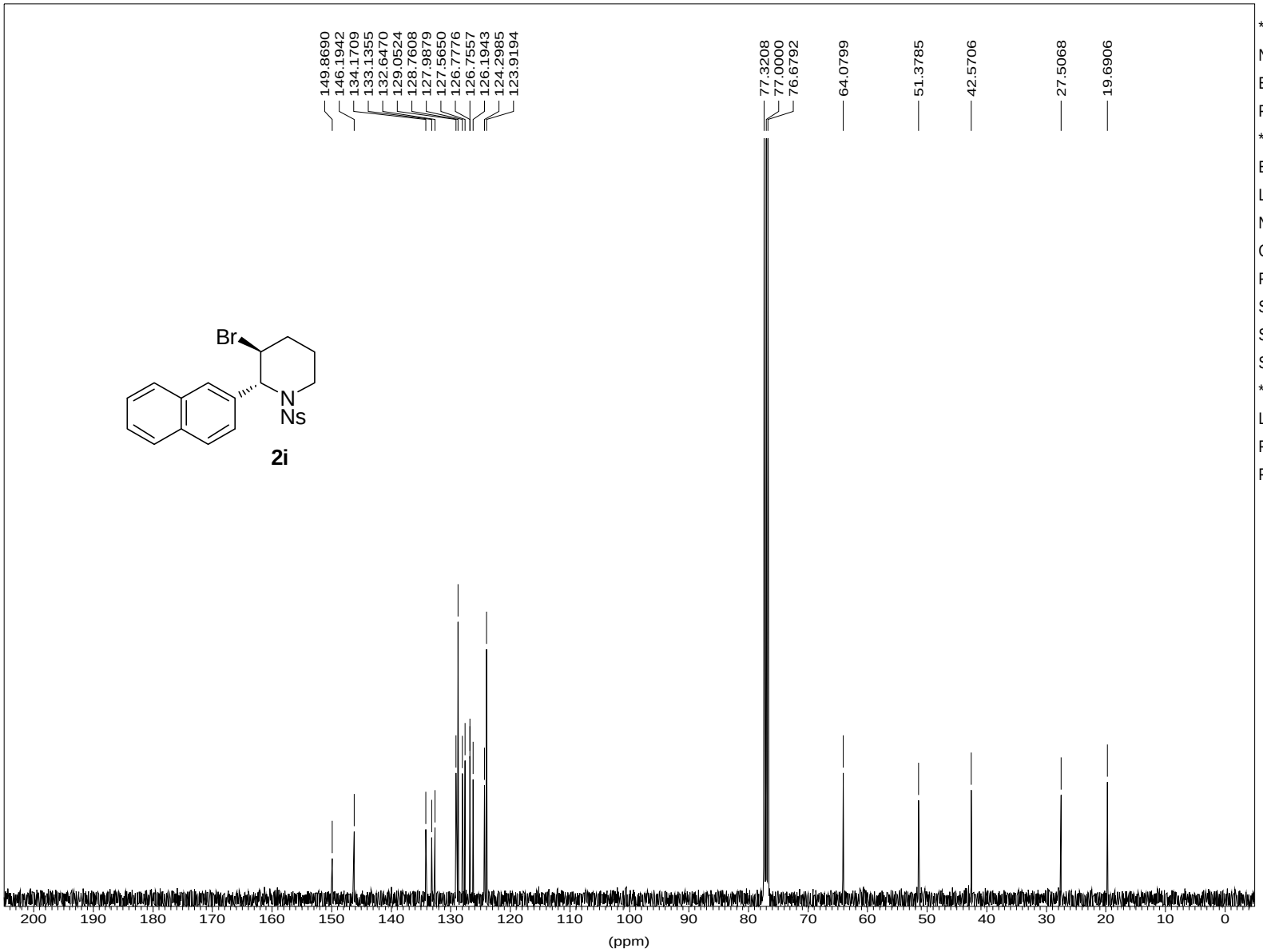
*** Acquisition Parameters ***

BF1	:	500.2300000 MHz
LOCNUC	:	2H
NS	:	8
O1	:	2751.27 Hz
PULPROG	:	zg
SFO1	:	500.2327513 MHz
SOLVENT	:	CDCl3
SW	:	15.0080 ppm

*** Processing Parameters ***

LB	:	0.10 Hz
PHC0	:	419.575 degre
PHC1	:	-7.498 degre

2-naph-P



*** Current Data Parameters ***

NAME	:	dec09zl
EXPNO	:	4
PROCNO	:	1

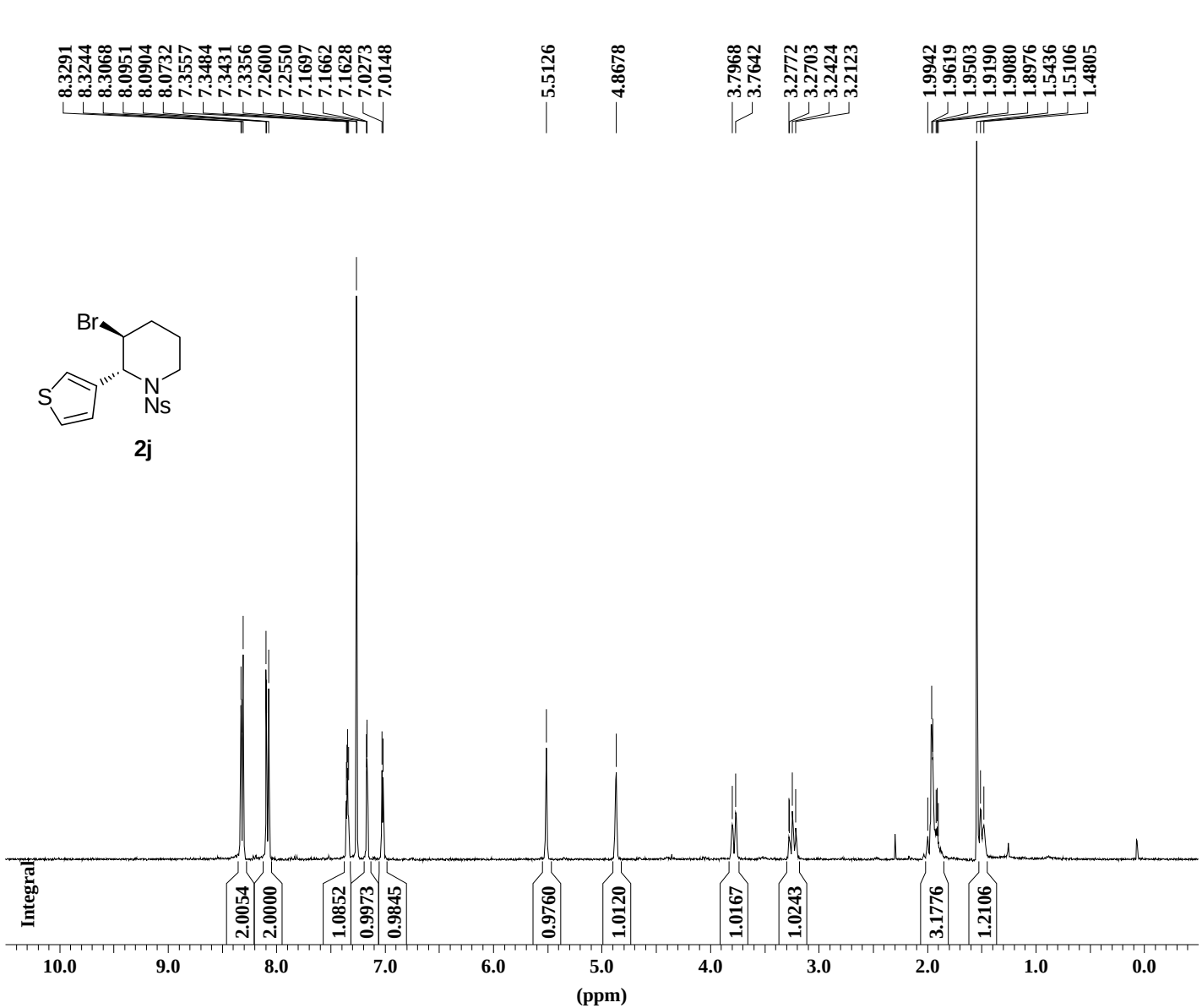
*** Acquisition Parameters ***

BF1	:	100.6127690 MHz
LOCNUC	:	2H
NS	:	1024
O1	:	11067.40 Hz
PULPROG	:	zgpg30
SFO1	:	100.6238364 MHz
SOLVENT	:	CDCl3
SW	:	238.8943 ppm

*** Processing Parameters ***

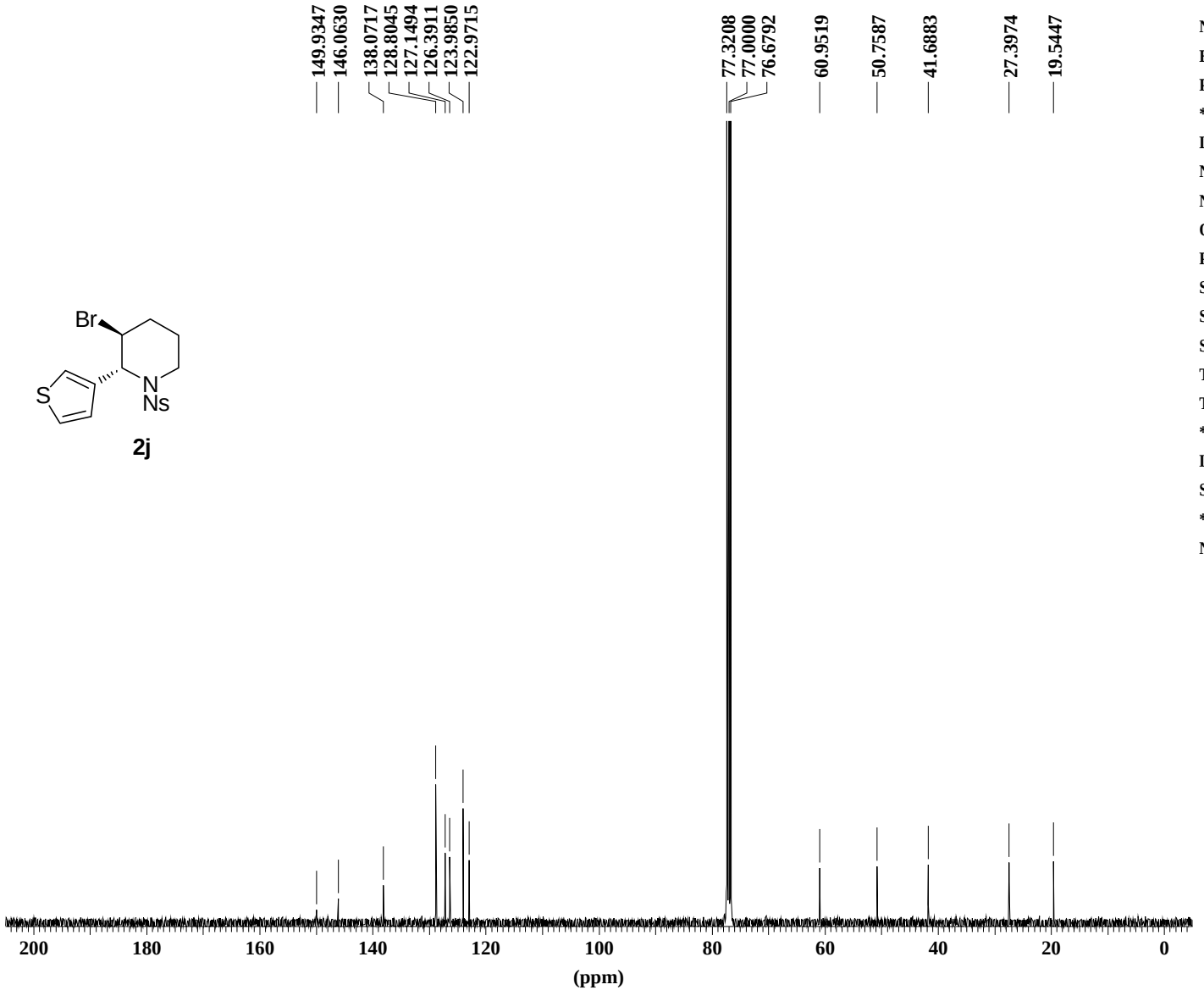
LB	:	1.00 Hz
PHC0	:	112.007 degree
PHC1	:	-72.371 degree

3203-10



*** Current Data Parameters ***
NAME : oct04zl
EXPNO : 1
PROCNO : 1
*** Acquisition Parameters ***
LOCNUC : 2H
NS : 8
NUCLEUS : off
O1 : 2470.97 Hz
PULPROG : zg30
SFO1 : 400.1324710 MHz
SOLVENT : CDCl3
SW : 20.5524 ppm
TD : 65536
TE : 299.9 K
*** Processing Parameters ***
LB : 0.30 Hz
SF : 400.1300100 MHz
*** 1D NMR Plot Parameters ***
NUCLEUS : off

3203-10



*** Current Data Parameters ***

NAME	:	oct04zl
EXPNO	:	2
PROCNO	:	1

*** Acquisition Parameters ***

LOCNUC	:	2H
NS	:	3266
NUCLEUS	:	off
O1	:	11067.40 Hz
PULPROG	:	zgpg30
SFO1	:	100.6238364 MHz
SOLVENT	:	CDCl3
SW	:	238.8943 ppm
TD	:	65536
TE	:	300.4 K

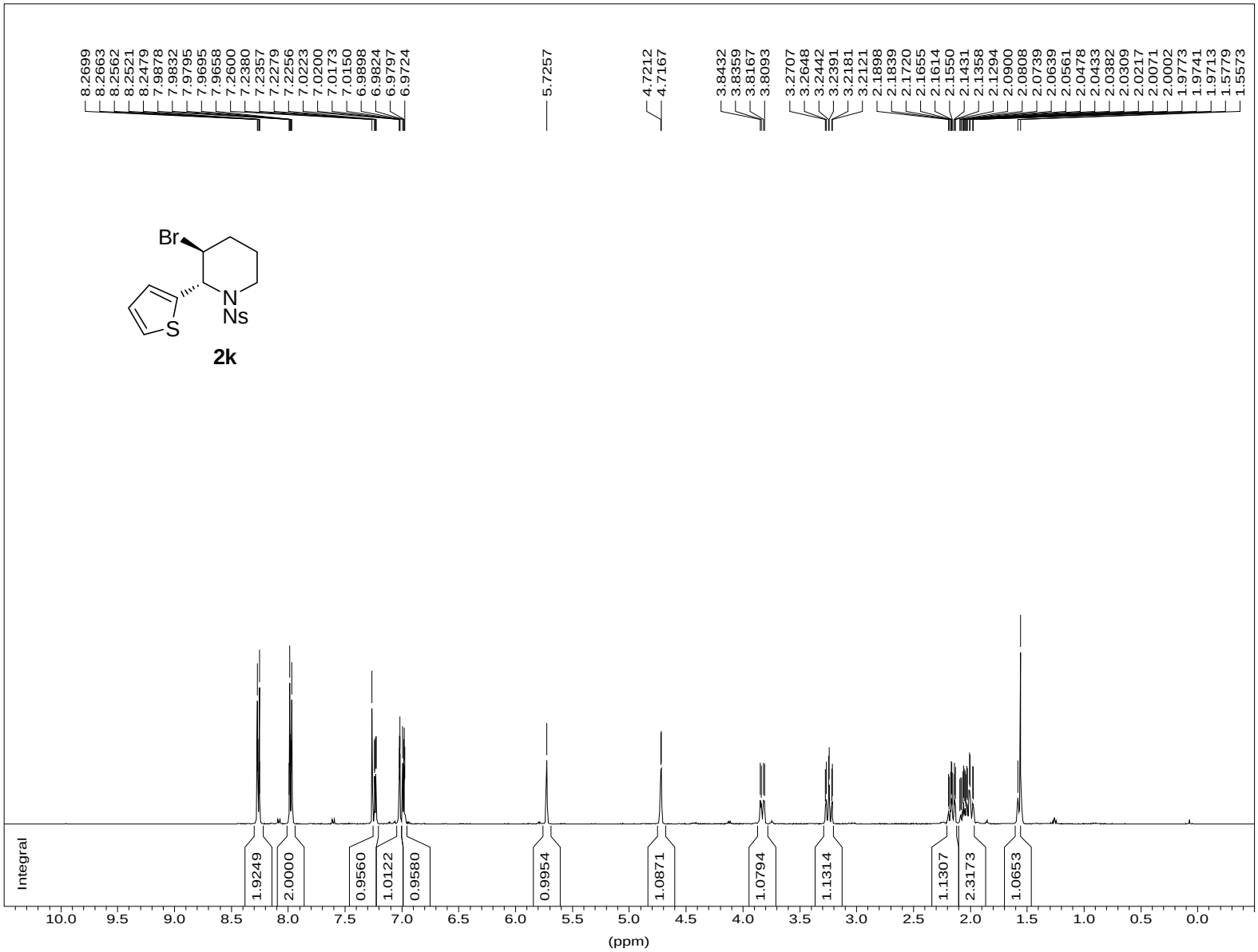
*** Processing Parameters ***

LB	:	1.00 Hz
SF	:	100.6127700 MHz

*** 1D NMR Plot Parameters ***

NUCLEUS	:	off

3203-9



*** Current Data Parameters ***

NAME	:	zl10-03
EXPNO	:	1
PROCNO	:	1

*** Acquisition Parameters ***

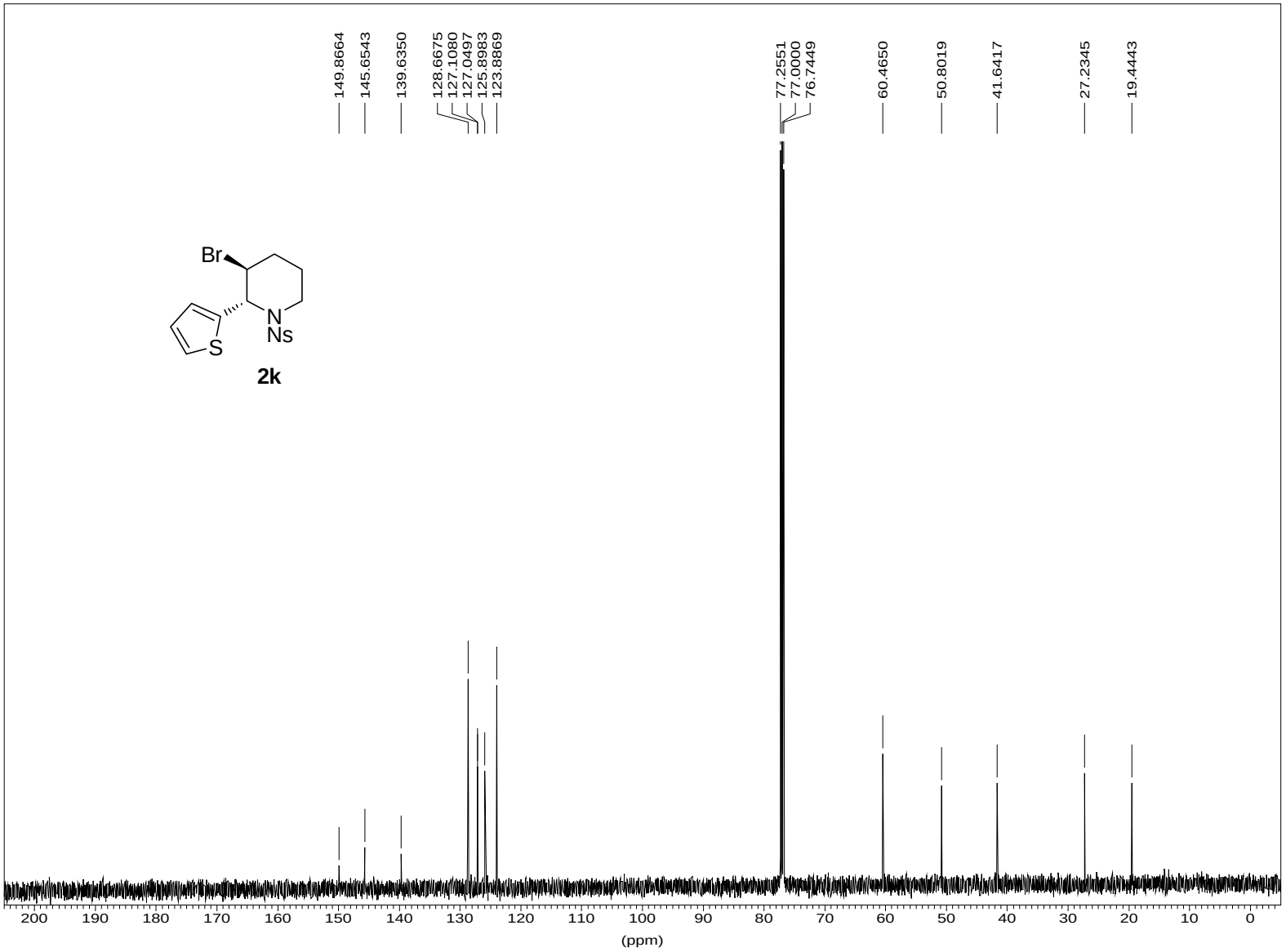
BF1	:	500.2300000 MHz
LOCNUC	:	2H
NS	:	8
O1	:	2751.27 Hz
PULPROG	:	zg
SFO1	:	500.2327513 MHz
SOLVENT	:	CDCl3
SW	:	15.0080 ppm

*** Processing Parameters ***

LB	:	0.10 Hz
PHC0	:	405.396 degree
PHC1	:	-11.004 degree

13C AMX500

3203-9



*** Current Data Parameters ***

NAME	:	zl1003
EXPNO	:	8
PROCNO	:	1

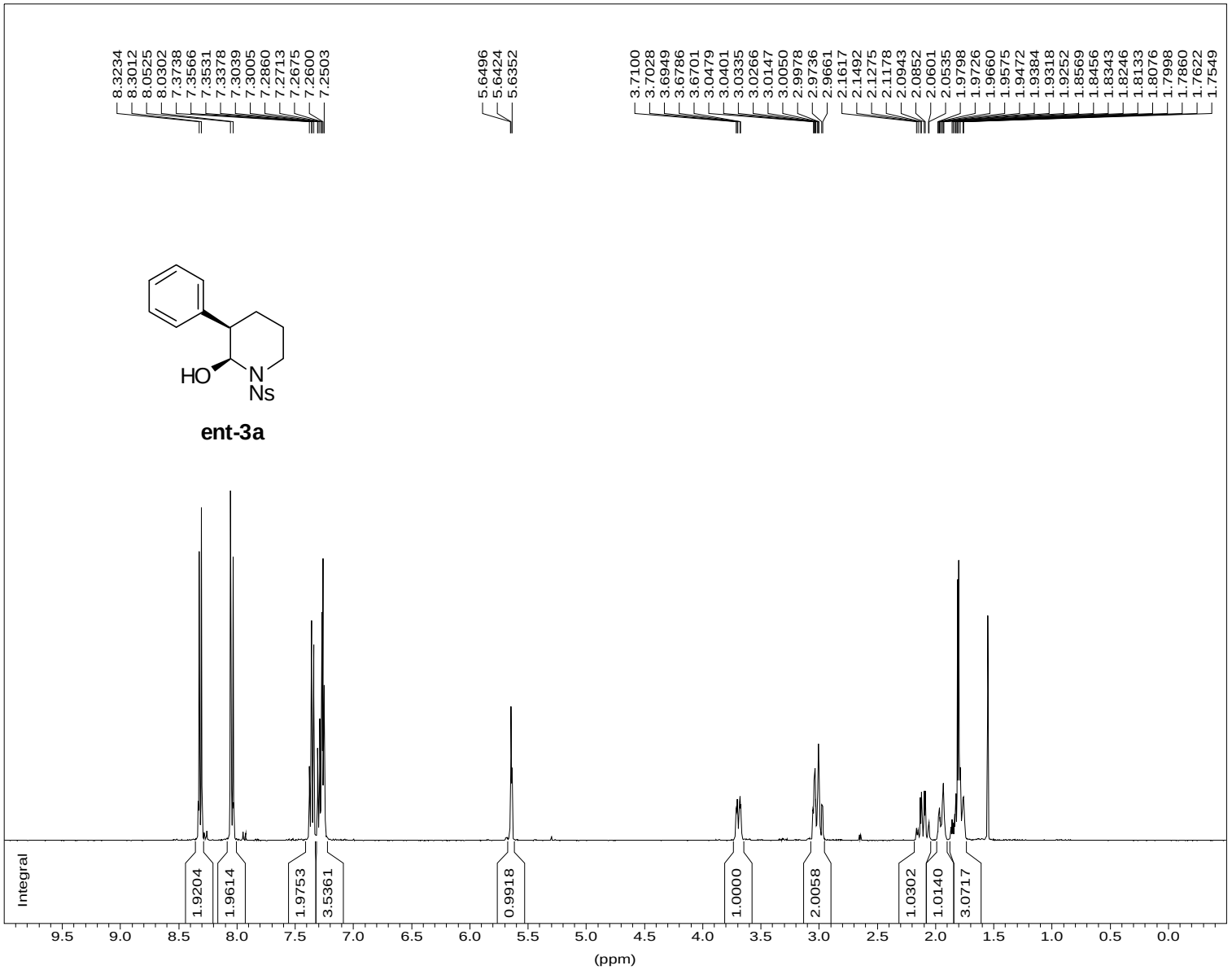
*** Acquisition Parameters ***

BF1	:	125.7577890 MHz
LOCNUC	:	2H
NS	:	246
O1	:	13204.57 Hz
PULPROG	:	zgpg30
SFO1	:	125.7709936 MHz
SOLVENT	:	CDCl3
SW	:	238.7675 ppm

*** Processing Parameters ***

LB	:	1.00 Hz
PHC0	:	230.027 degree
PHC1	:	17.928 degree

OH-U



*** Current Data Parameters ***

NAME	:	nov30zl
EXPNO	:	1
PROCNO	:	1

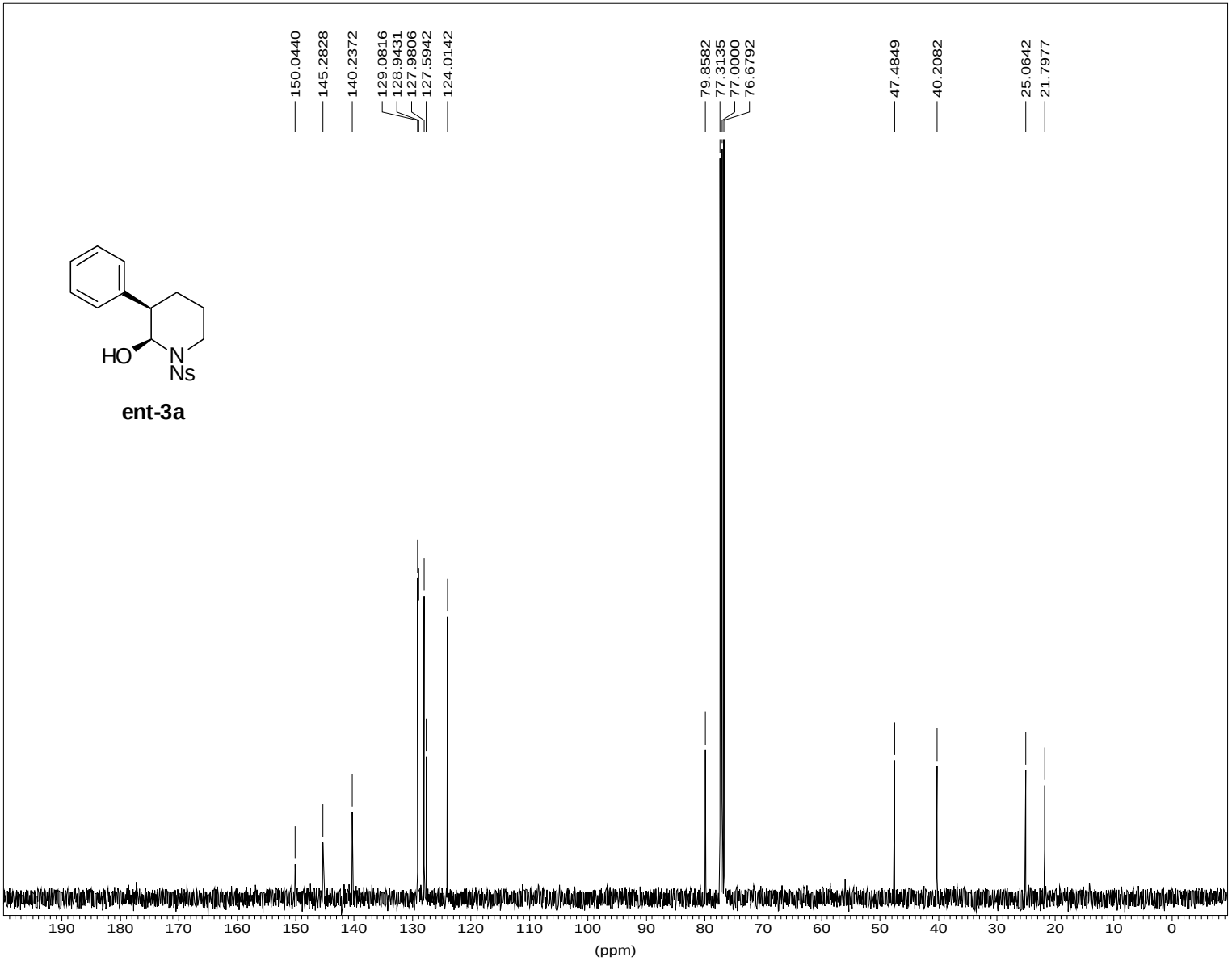
*** Acquisition Parameters ***

BF1	:	400.1300000 MHz
LOCNUC	:	2H
NS	:	8
O1	:	2470.97 Hz
PULPROG	:	zg30
SFO1	:	400.1324710 MHz
SOLVENT	:	CDCl3
SW	:	20.5524 ppm

*** Processing Parameters ***

LB	:	0.30 Hz
PHC0	:	-49.651 degree
PHC1	:	-20.218 degree

OH-U



*** Current Data Parameters ***

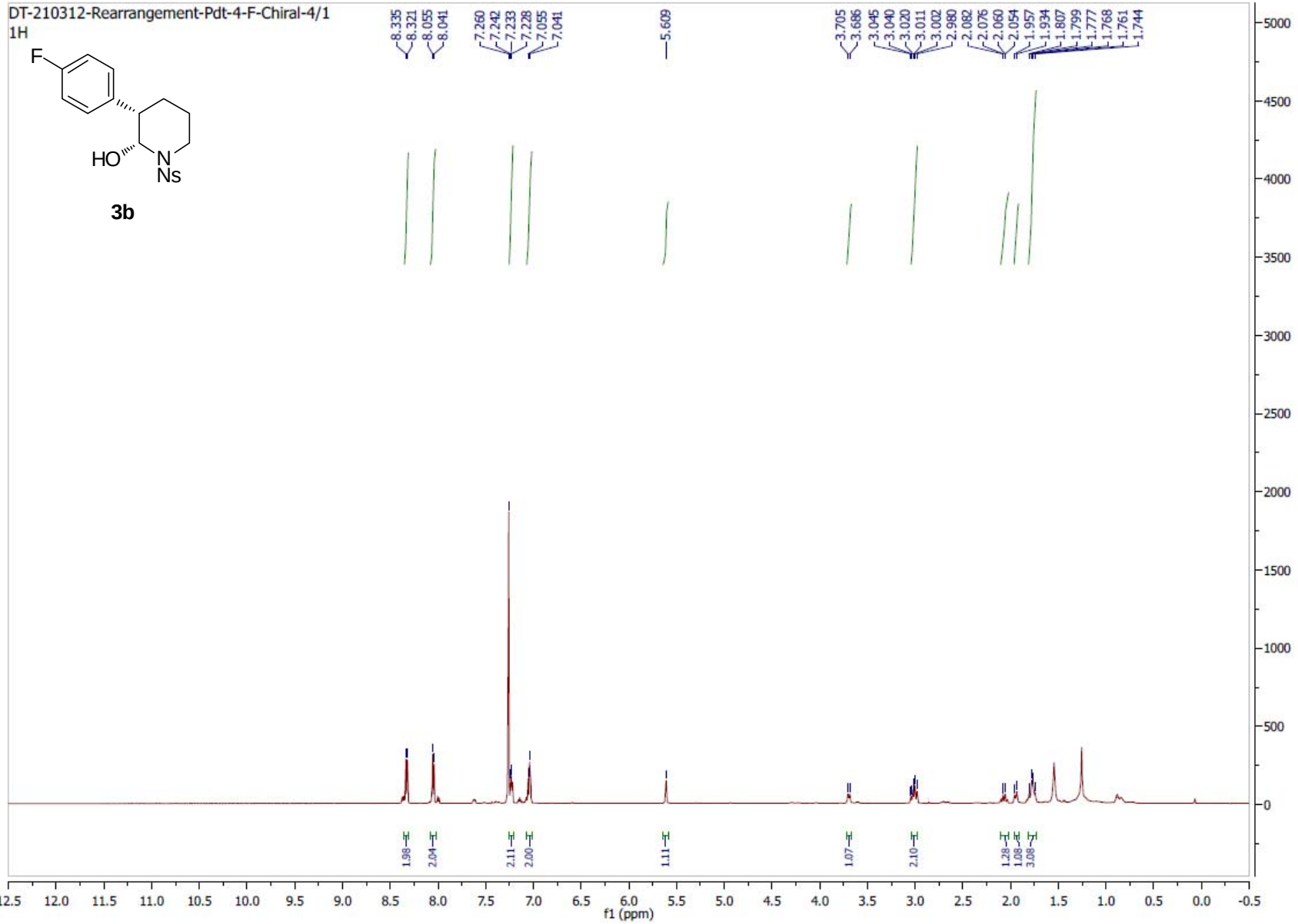
NAME	:	nov30zl
EXPNO	:	6
PROCNO	:	1

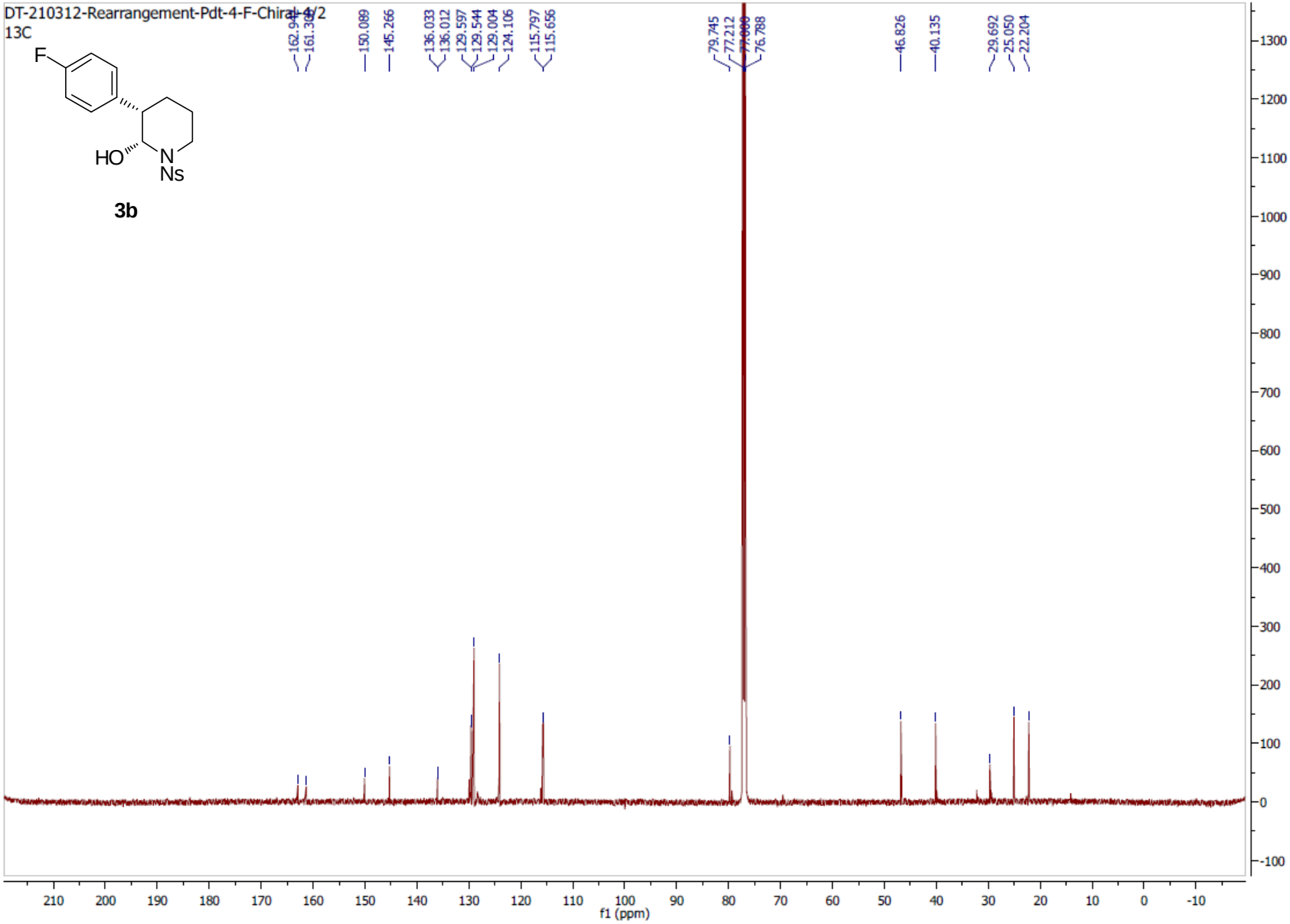
*** Acquisition Parameters ***

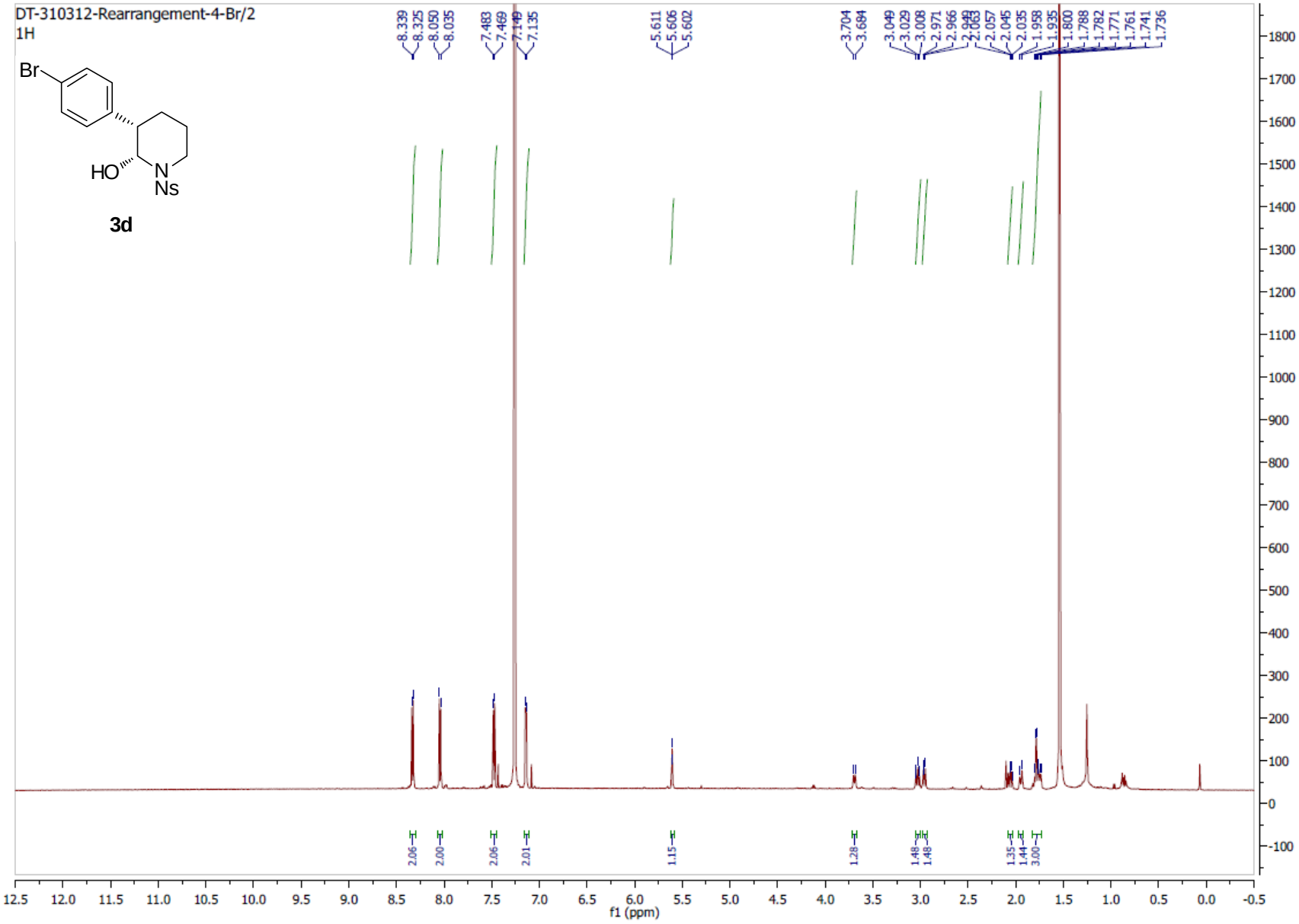
BF1	:	100.6127690 MHz
LOCNUC	:	2H
NS	:	205
O1	:	11067.40 Hz
PULPROG	:	zgpg30
SFO1	:	100.6238364 MHz
SOLVENT	:	CDCl3
SW	:	238.8943 ppm

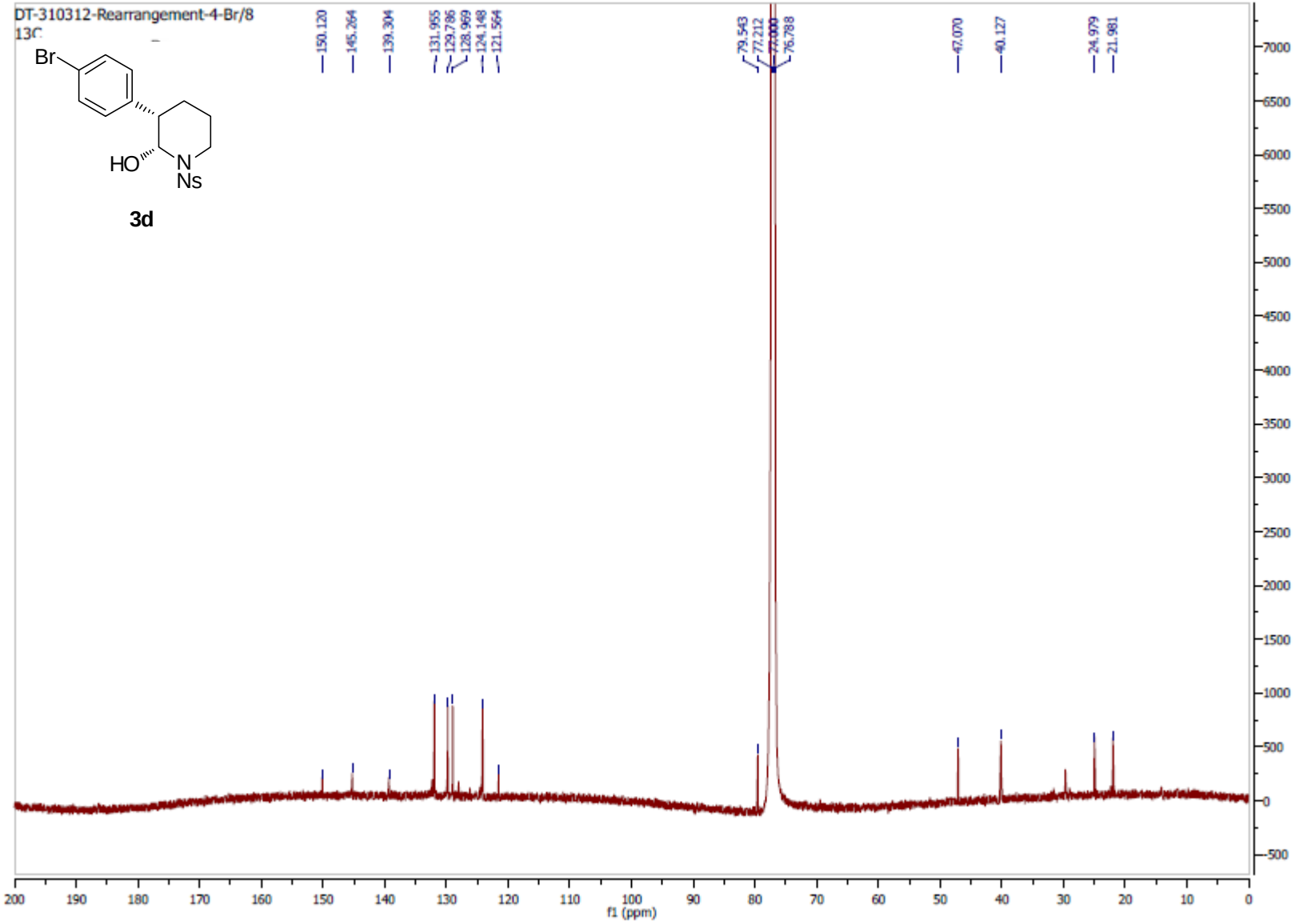
*** Processing Parameters ***

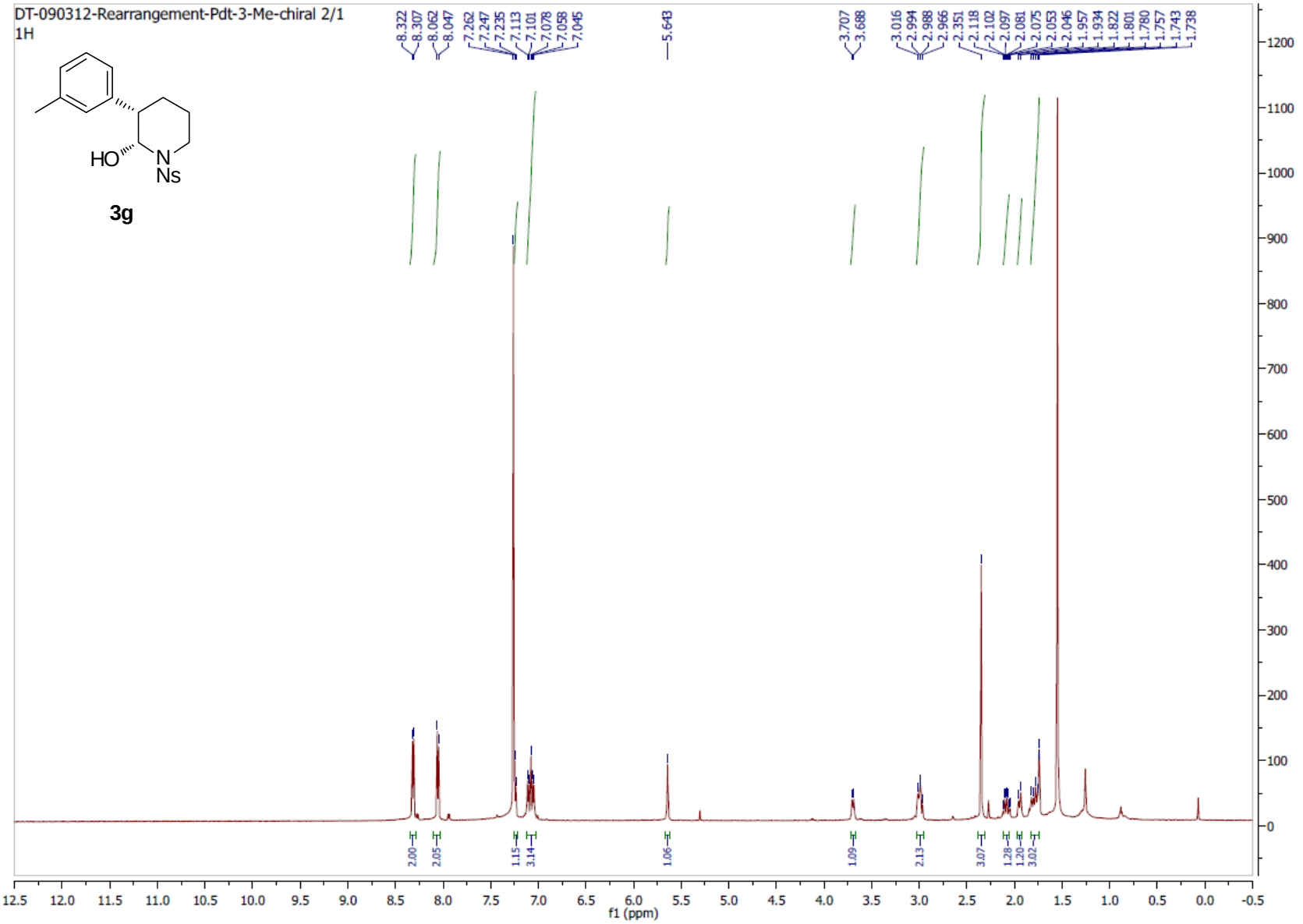
LB	:	1.00 Hz
PHC0	:	96.423 degree
PHC1	:	-51.530 degree

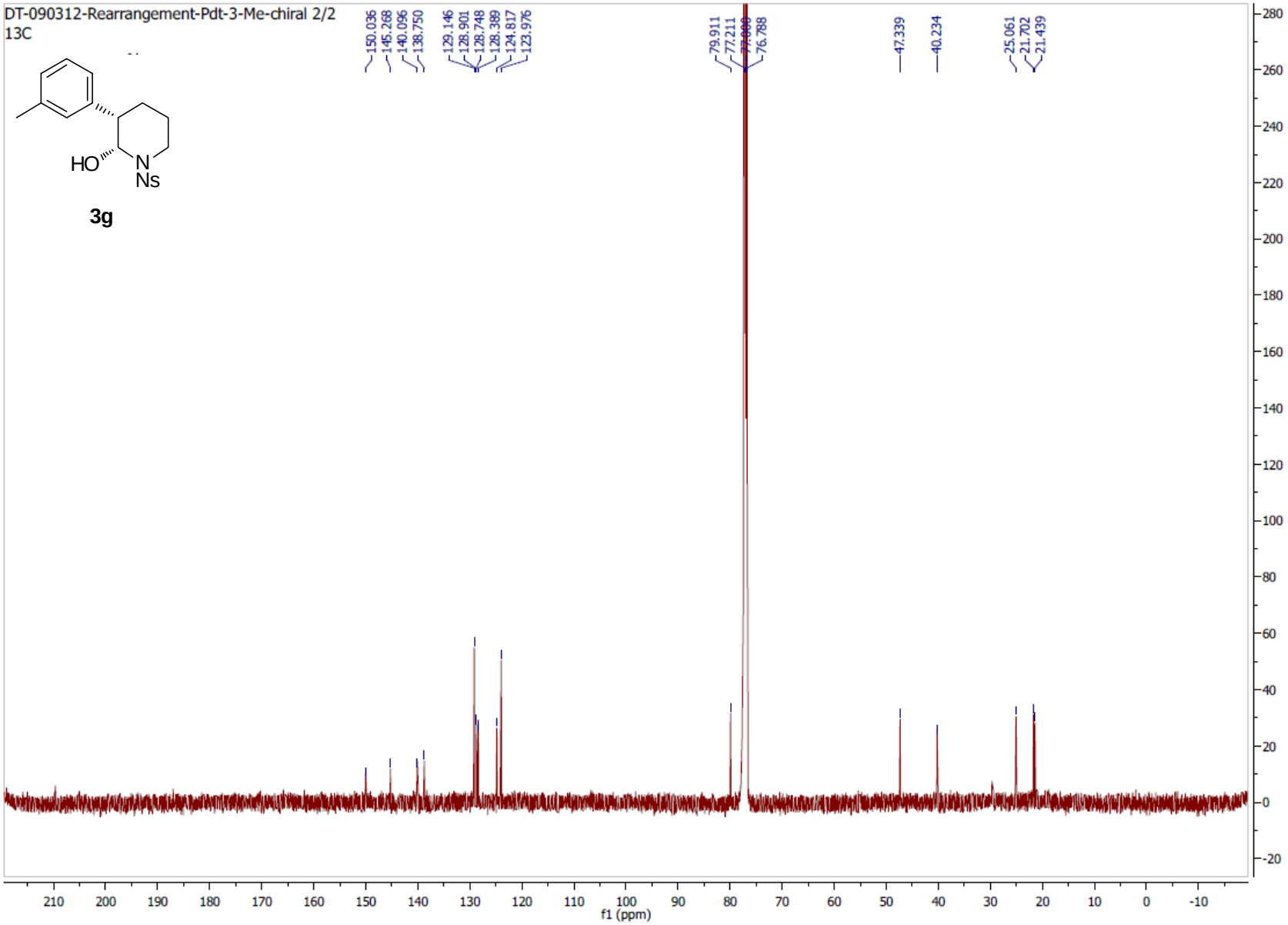

DT-210312-Rearrangement-Pdt-4-F-Chiral-4/1
1H
F
HO
N
Ns
3b
8.335
8.321
8.055
8.041
7.260
7.242
7.233
7.228
7.055
7.041
5.609
3.705
3.686
3.045
3.040
3.020
3.011
3.002
2.980
2.082
2.076
2.060
2.054
1.957
1.934
1.807
1.799
1.777
1.768
1.761
1.744
1.98
2.04
2.11
2.00
1.11
1.07
2.10
1.28
1.08
3.08
f1 (ppm)


DT-210312-Rearrangement-Pdt-4-F-Chiral-4/2
13C
F
HO
N
Ns
3b
150.089
145.266
136.033
136.012
129.597
129.544
129.004
124.106
115.797
115.656
79.745
77.212
76.788
46.826
40.135
29.692
25.050
22.204
f1 (ppm)

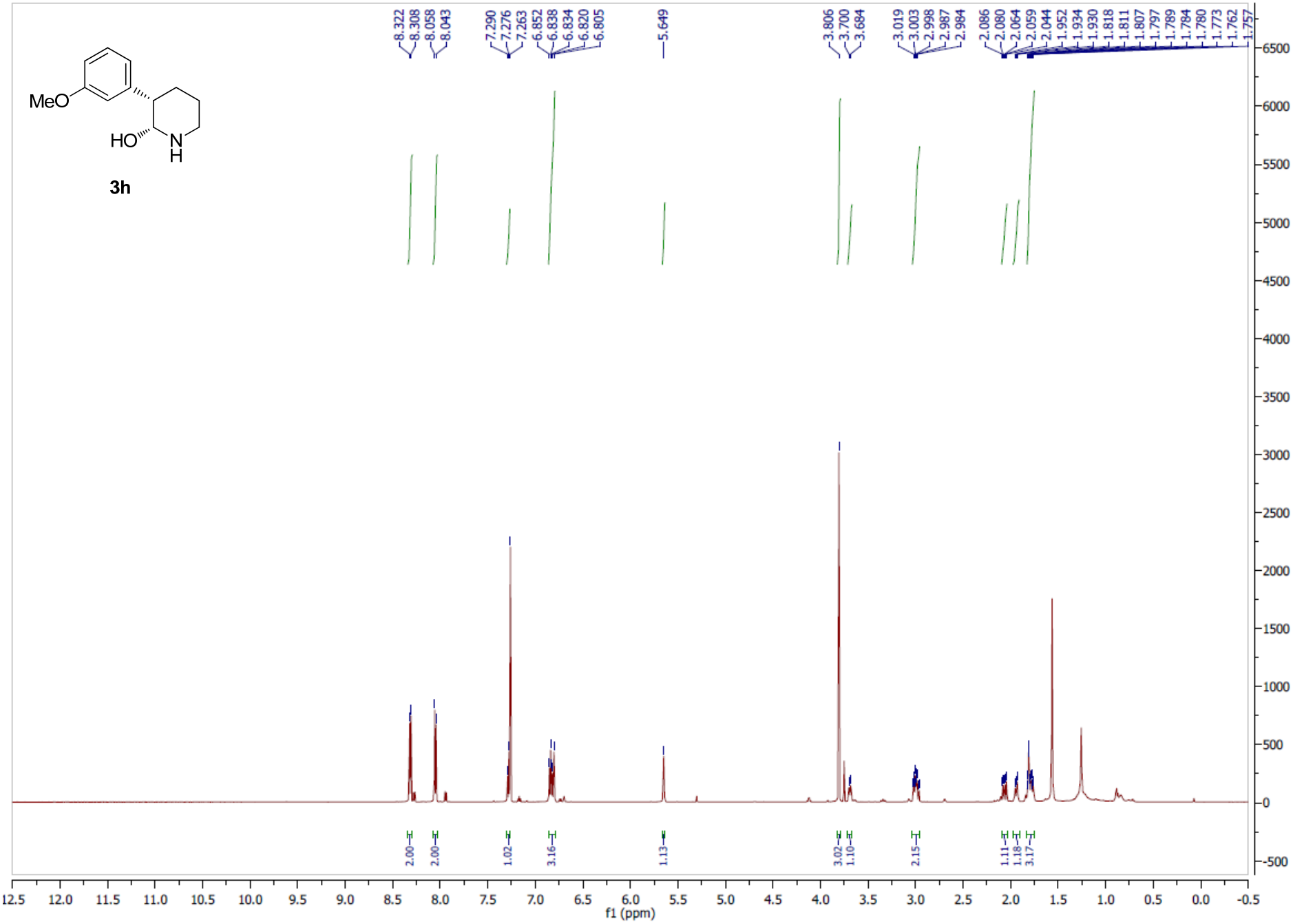

DT-310312-Rearrangement-4-Br/2
1H
Br
HO
N
Ns
3d
8.339
8.325
8.050
8.035
7.483
7.469
7.149
7.135
5.611
5.606
5.602
3.704
3.684
3.049
3.029
3.008
2.971
2.966
2.949
2.063
2.057
2.045
2.035
1.958
1.935
1.800
1.788
1.782
1.771
1.761
1.741
1.736
2.06
2.00
2.06
2.01
1.15
1.28
1.48
1.48
1.35
1.44
3.00
f1 (ppm)

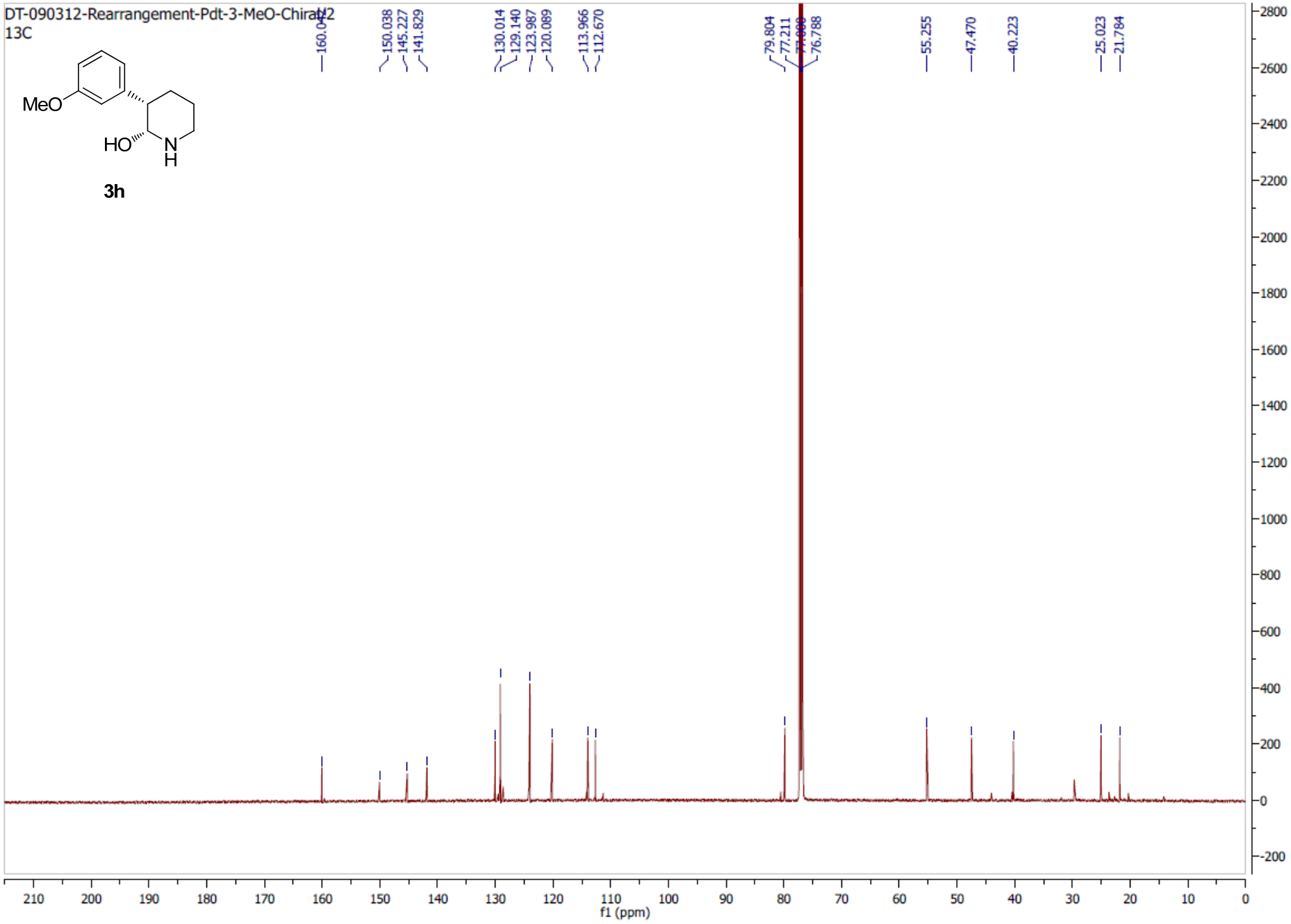

DT-310312-Rearrangement-4-Br/8
13C
Br
HO
N
Ns
3d
150.120
145.264
139.304
131.955
129.786
128.969
124.148
121.564
79.543
77.212
77.000
76.788
47.070
40.127
24.979
21.981
f1 (ppm)


DT-090312-Rearrangement-Pdt-3-Me-chiral 2/1
1H
HO
N
Ns
3g
8.322
8.307
8.062
8.047
7.262
7.247
7.235
7.113
7.101
7.078
7.058
7.045
5.643
3.707
3.688
3.016
2.994
2.988
2.966
2.351
2.118
2.102
2.097
2.081
2.075
2.053
2.046
1.957
1.934
1.822
1.801
1.780
1.757
1.743
1.738
2.00
2.05
1.15
3.14
1.06
1.09
2.13
3.07
1.28
1.20
3.02
f1 (ppm)

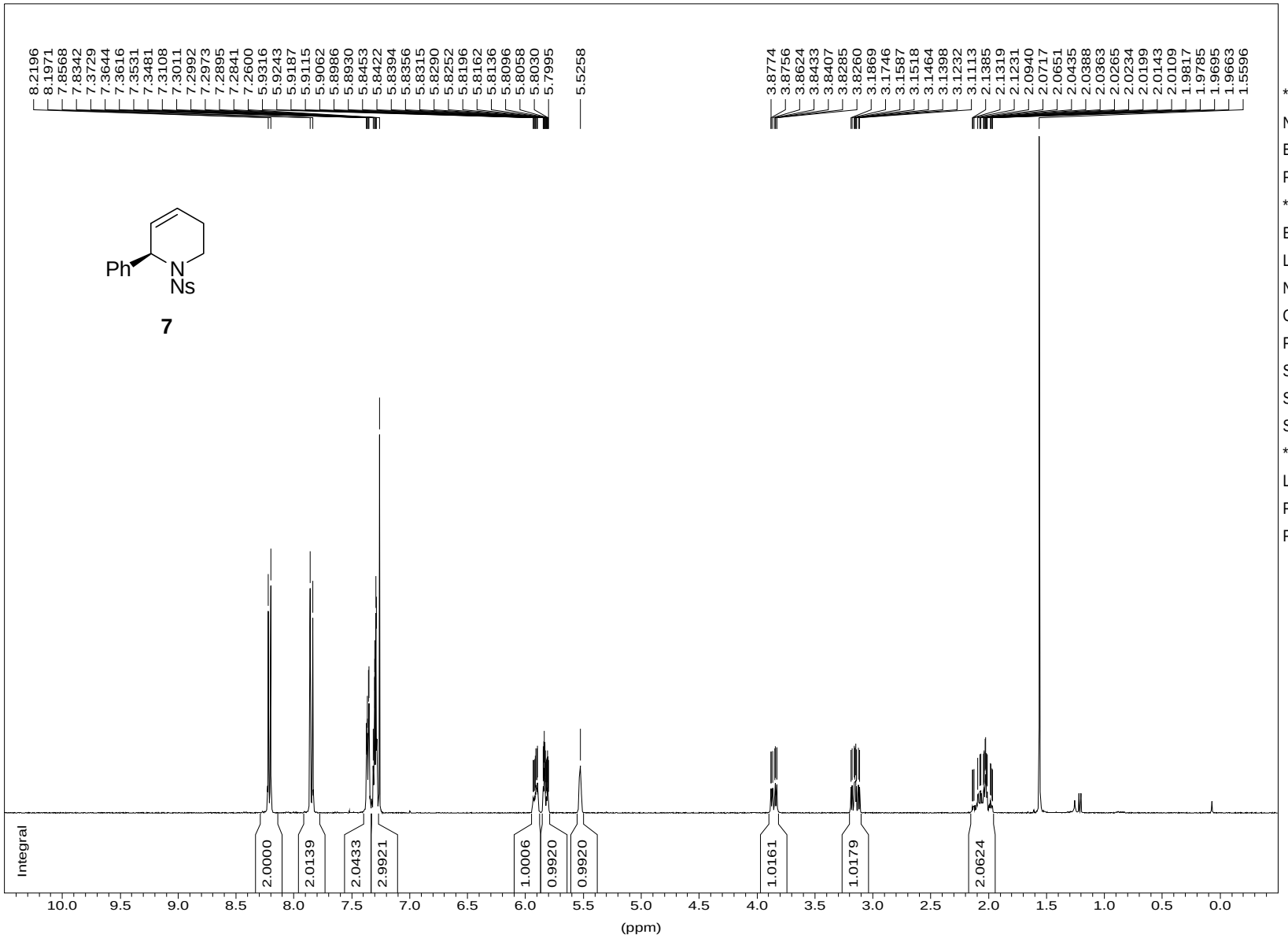

DT-090312-Rearrangement-Pdt-3-Me-chiral 2/2
13C
150.036
145.268
140.096
138.750
129.146
128.901
128.748
128.389
124.817
123.976
79.911
77.211
76.788
47.339
40.234
25.061
21.702
21.439
HO
N
Ns
f1 (ppm)

3g





3215U



7

*** Current Data Parameters ***

NAME	:	dec22zl
EXPNO	:	1
PROCNO	:	1

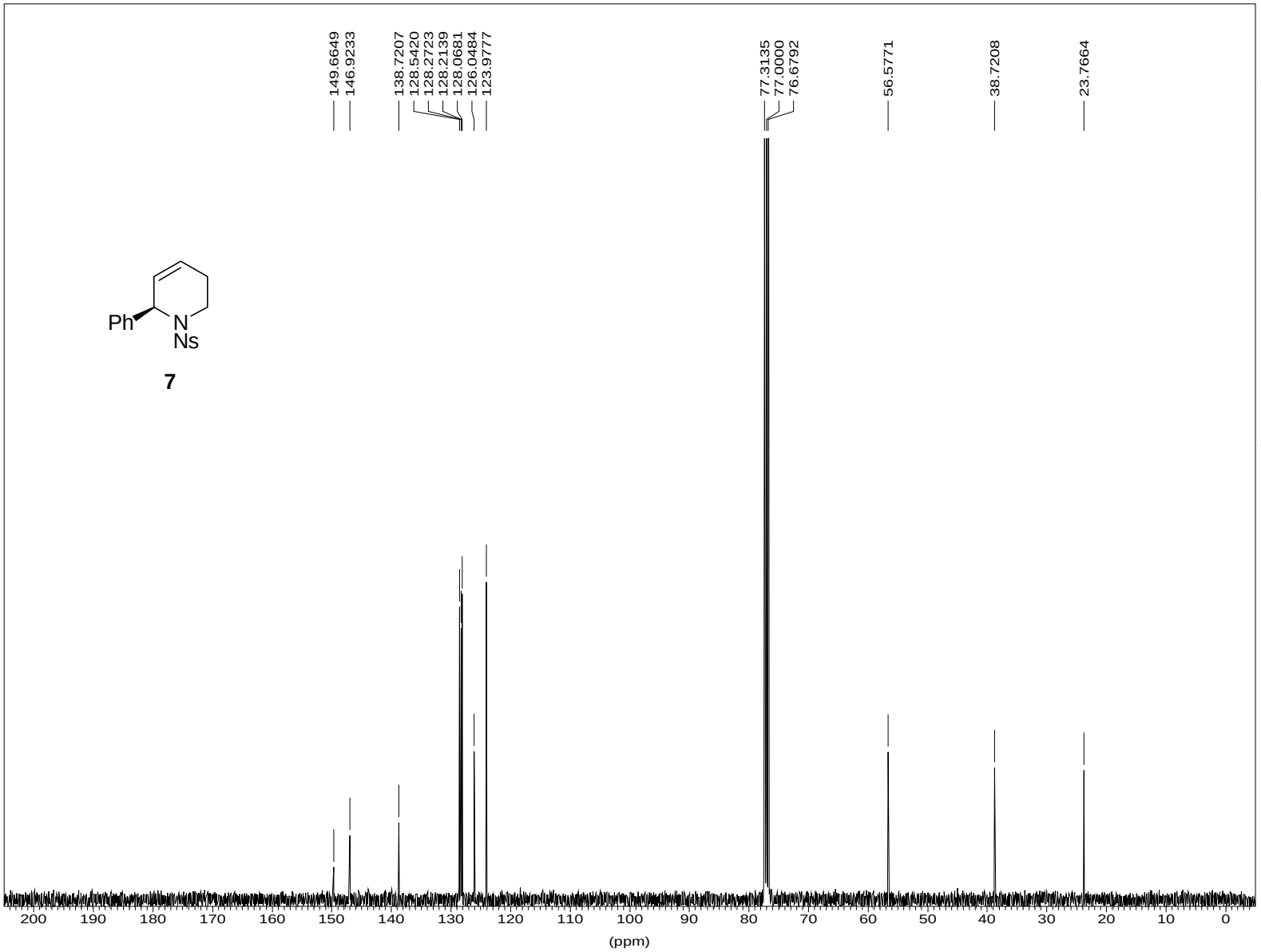
*** Acquisition Parameters ***

BF1	:	400.1300000 MHz
LOCNUC	:	2H
NS	:	8
O1	:	2470.97 Hz
PULPROG	:	zg30
SFO1	:	400.1324710 MHz
SOLVENT	:	CDCl3
SW	:	20.5524 ppm

*** Processing Parameters ***

LB	:	0.30 Hz
PHC0	:	-52.611 degree
PHC1	:	-17.064 degree

3215U



*** Current Data Parameters ***

NAME	:	dec22zl
EXPNO	:	2
PROCNO	:	1

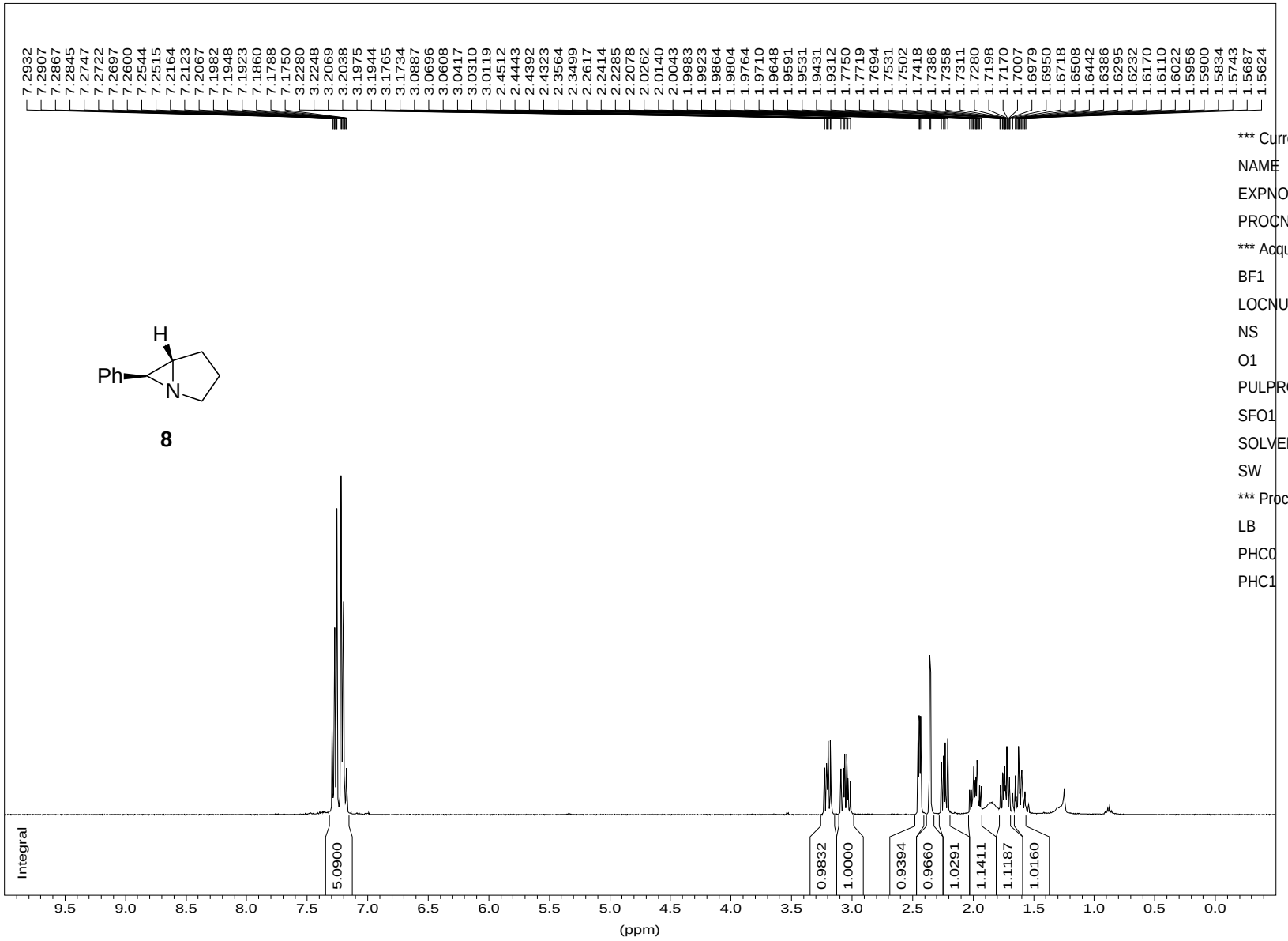
*** Acquisition Parameters ***

BF1	:	100.6127690 MHz
LOCNUC	:	2H
NS	:	1024
O1	:	11067.40 Hz
PULPROG	:	zgpg30
SFO1	:	100.6238364 MHz
SOLVENT	:	CDCl3
SW	:	238.8943 ppm

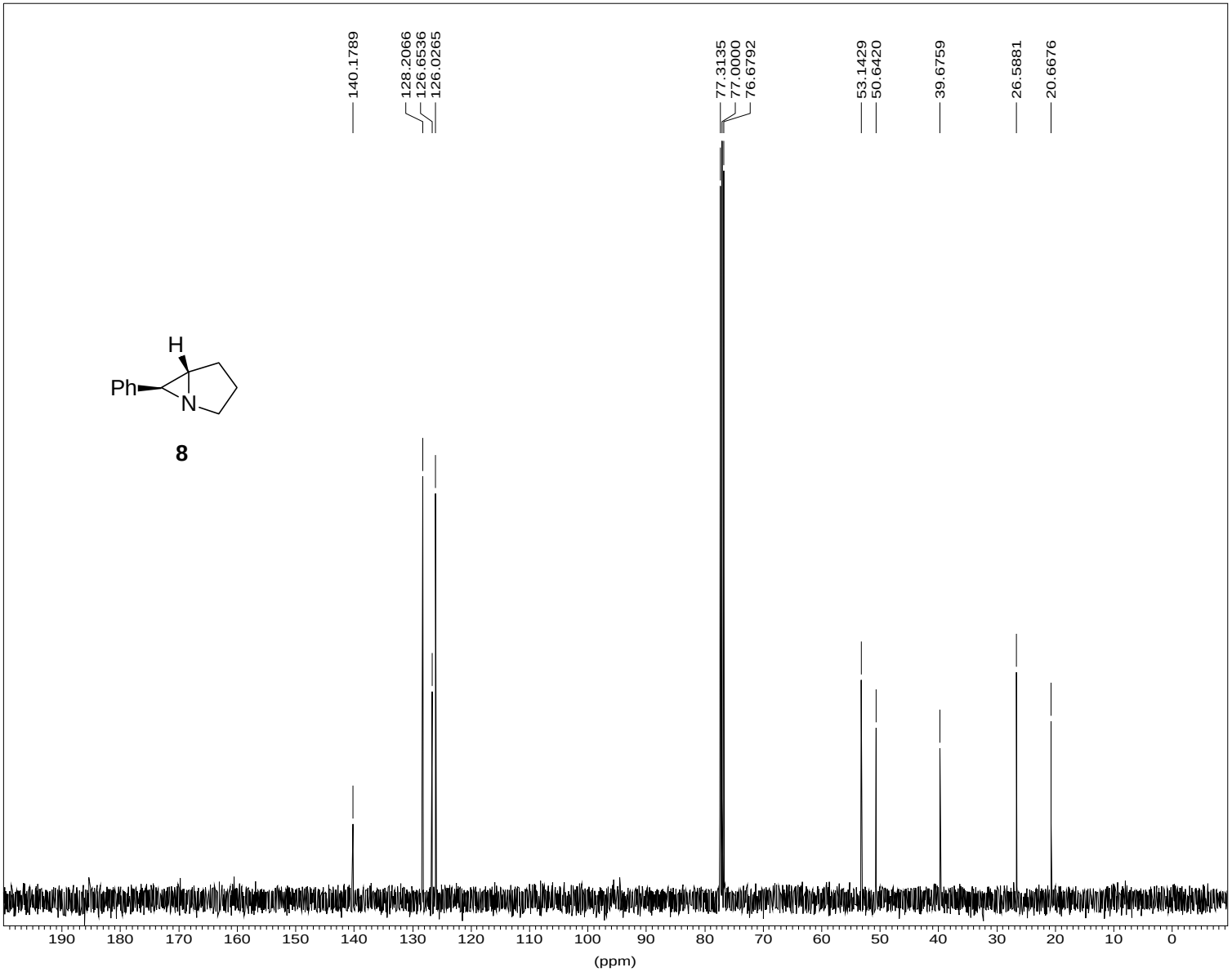
*** Processing Parameters ***

LB	:	1.00 Hz
PHC0	:	82.374 degree
PHC1	:	-44.722 degree

D



D



*** Current Data Parameters ***

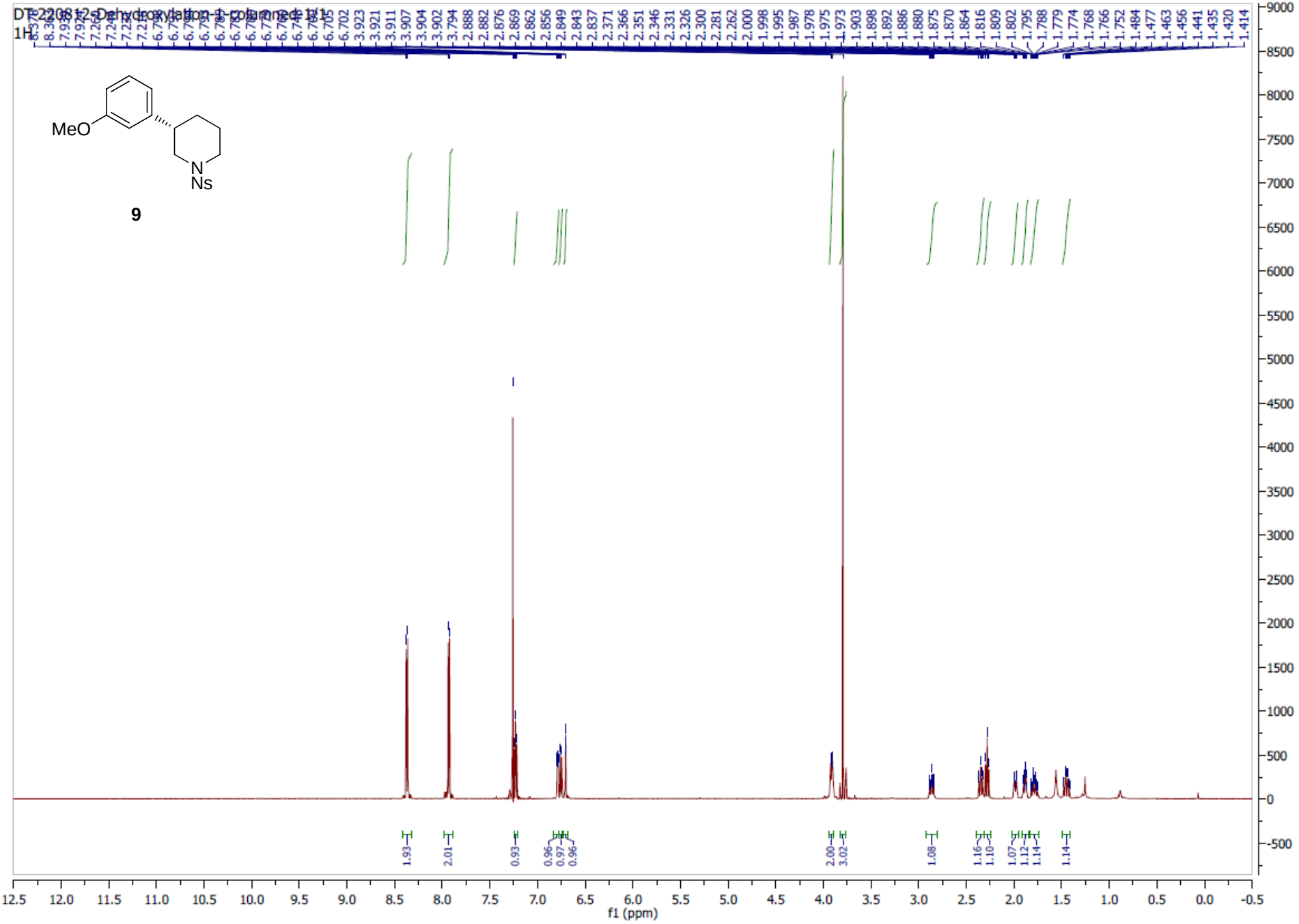
NAME	:	nov02zl
EXPNO	:	6
PROCNO	:	1

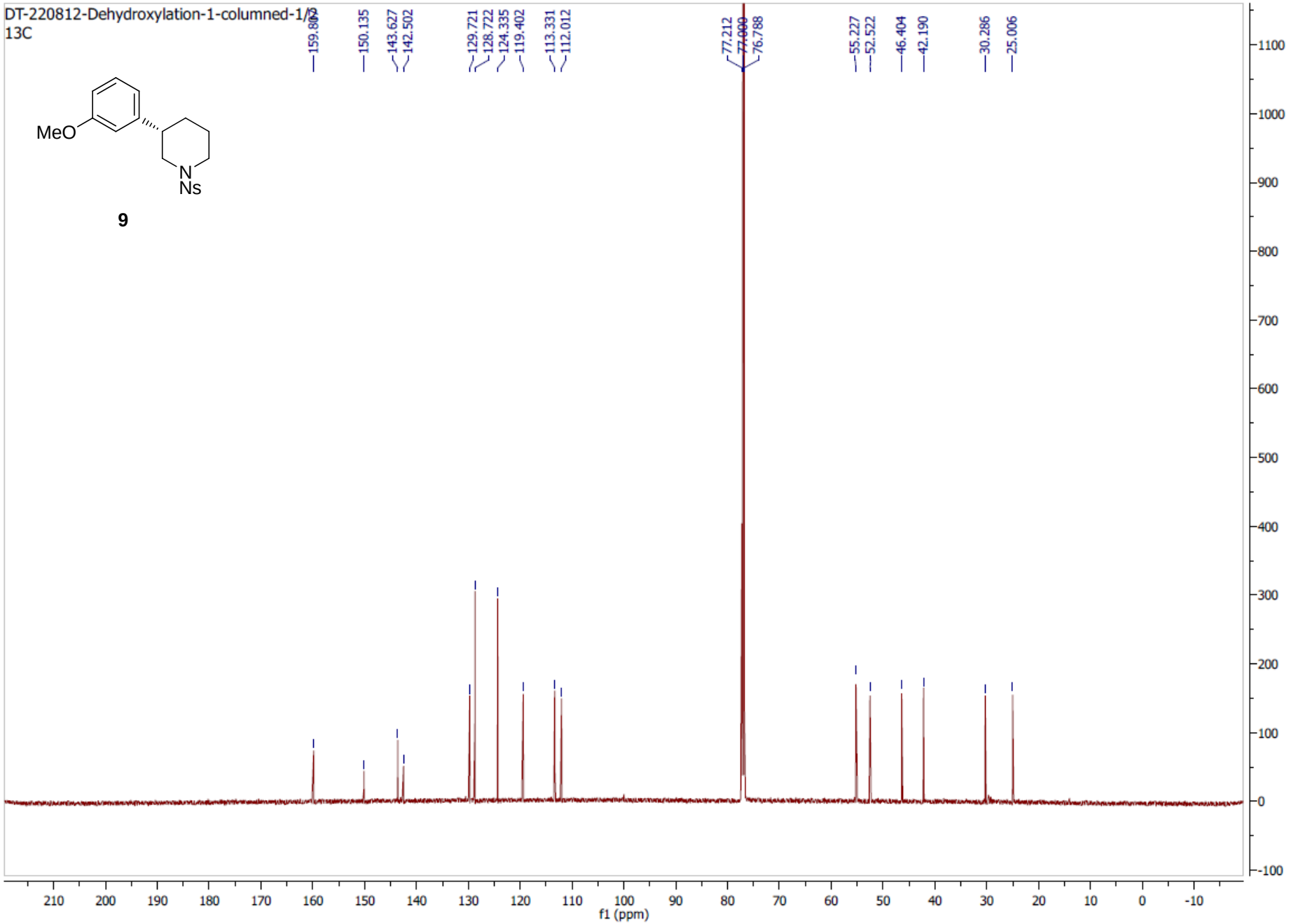
*** Acquisition Parameters ***

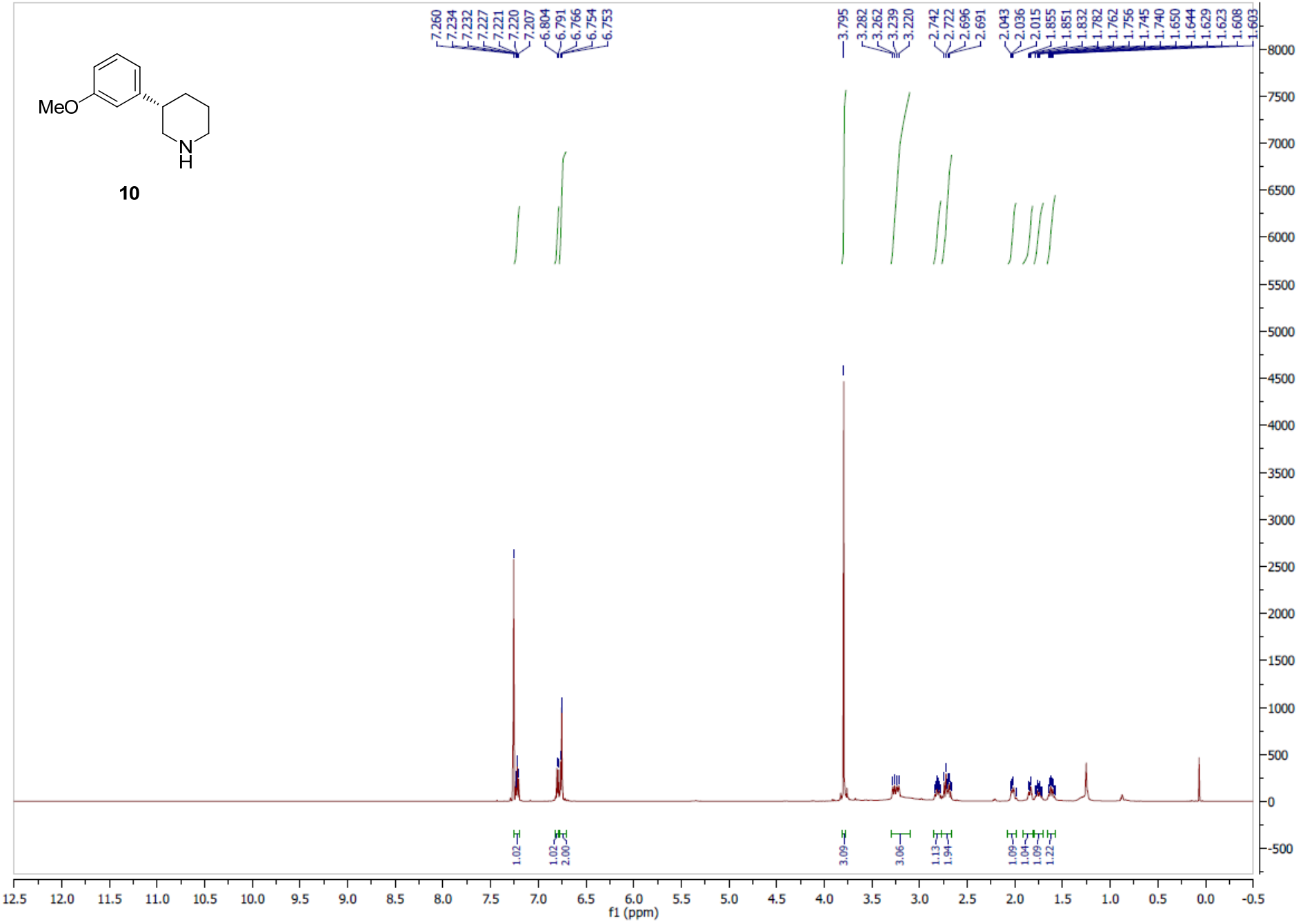
BF1	:	100.6127690 MHz
LOCNUC	:	2H
NS	:	93
O1	:	11067.40 Hz
PULPROG	:	zgpg30
SFO1	:	100.6238364 MHz
SOLVENT	:	CDCl3
SW	:	238.8943 ppm

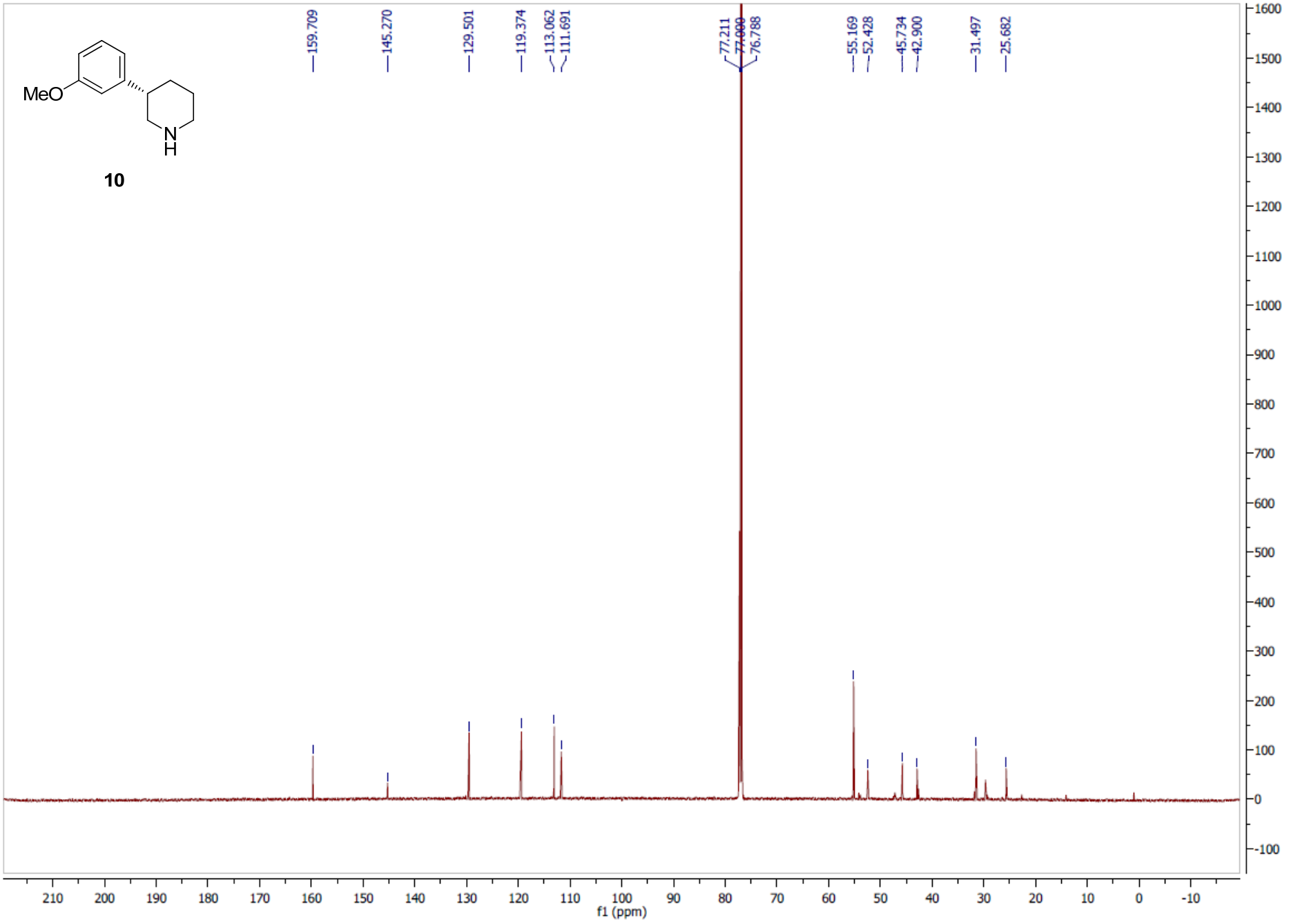
*** Processing Parameters ***

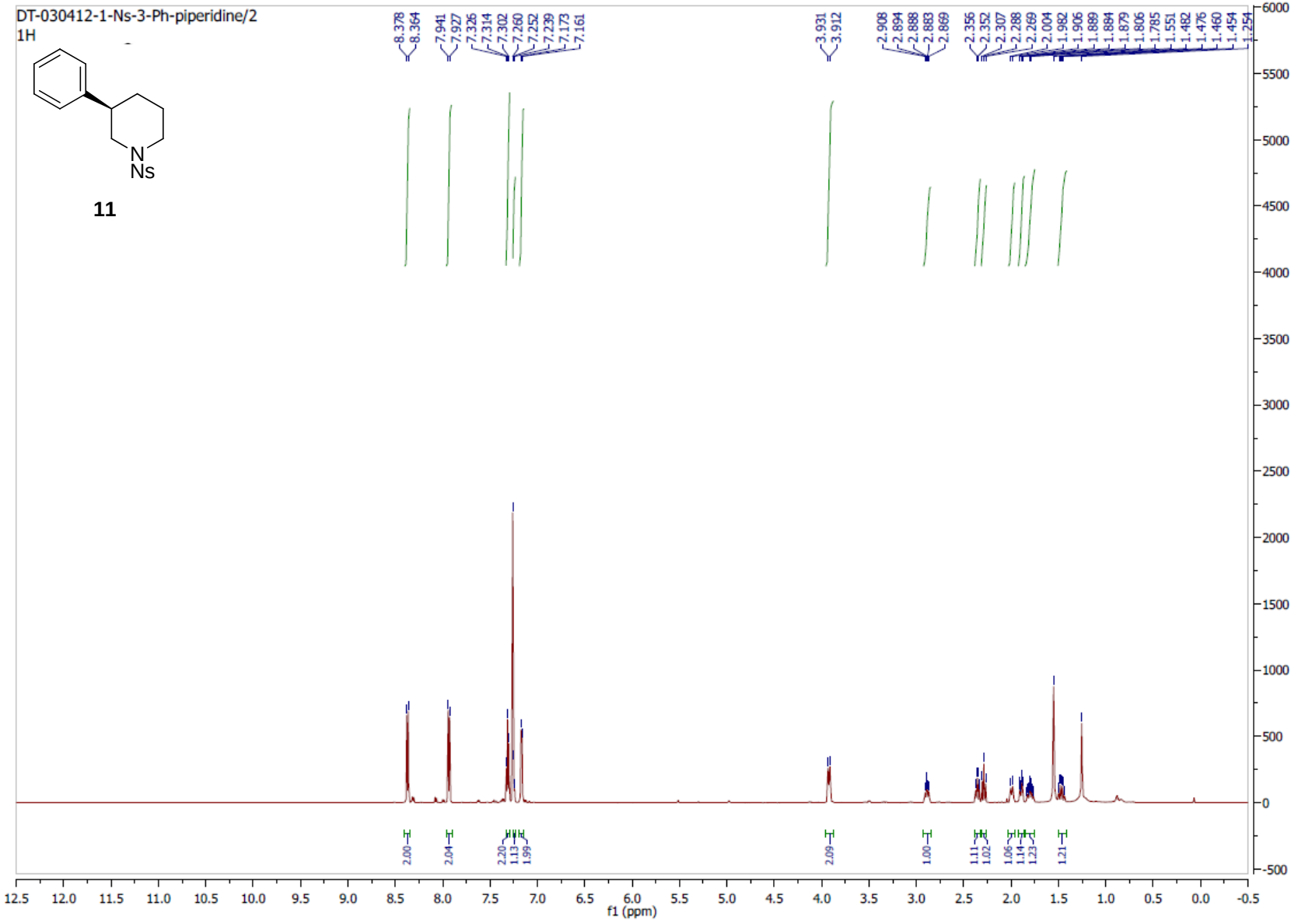
LB	:	1.00 Hz
PHC0	:	93.411 degree
PHC1	:	-45.328 degree

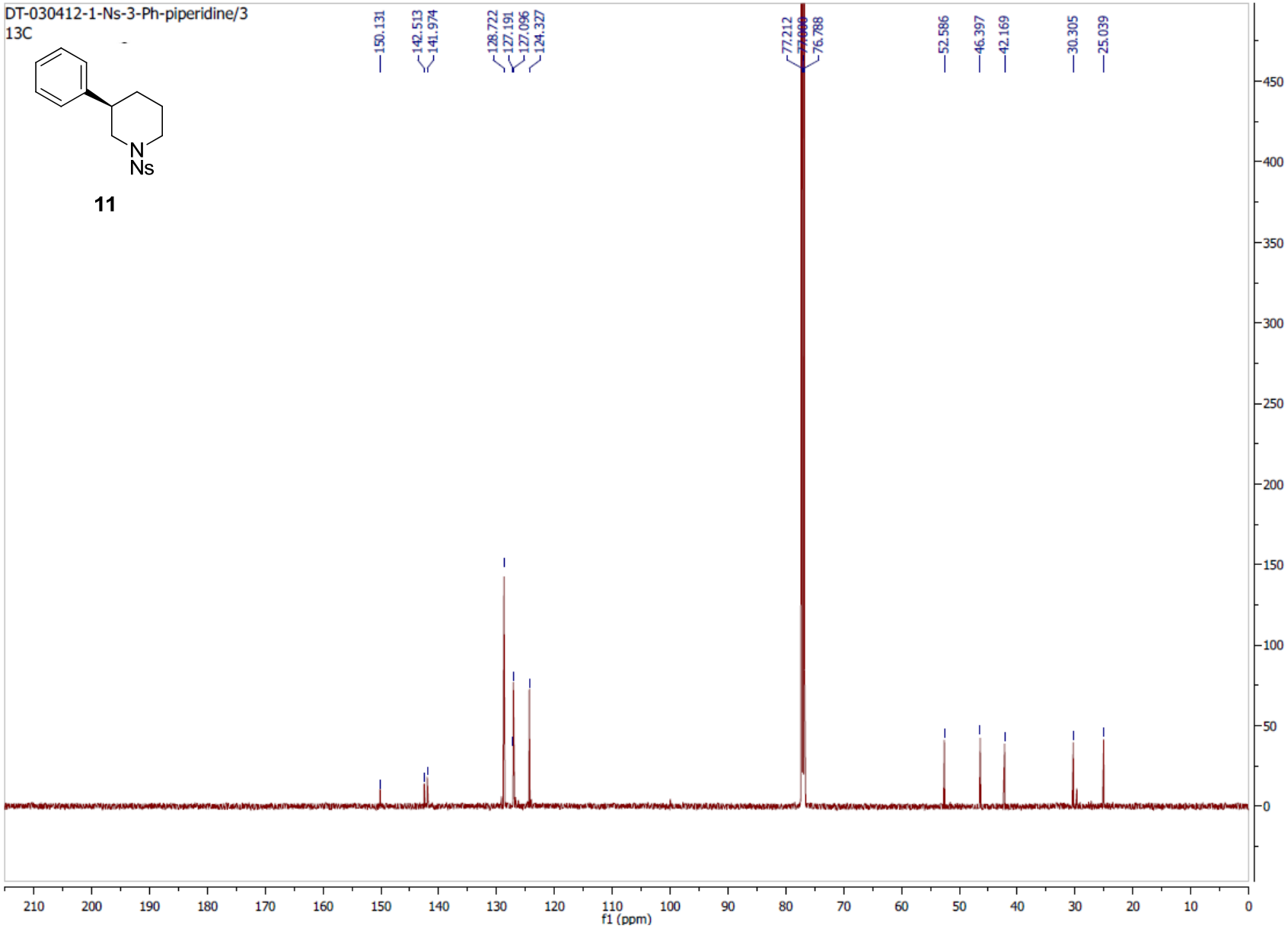




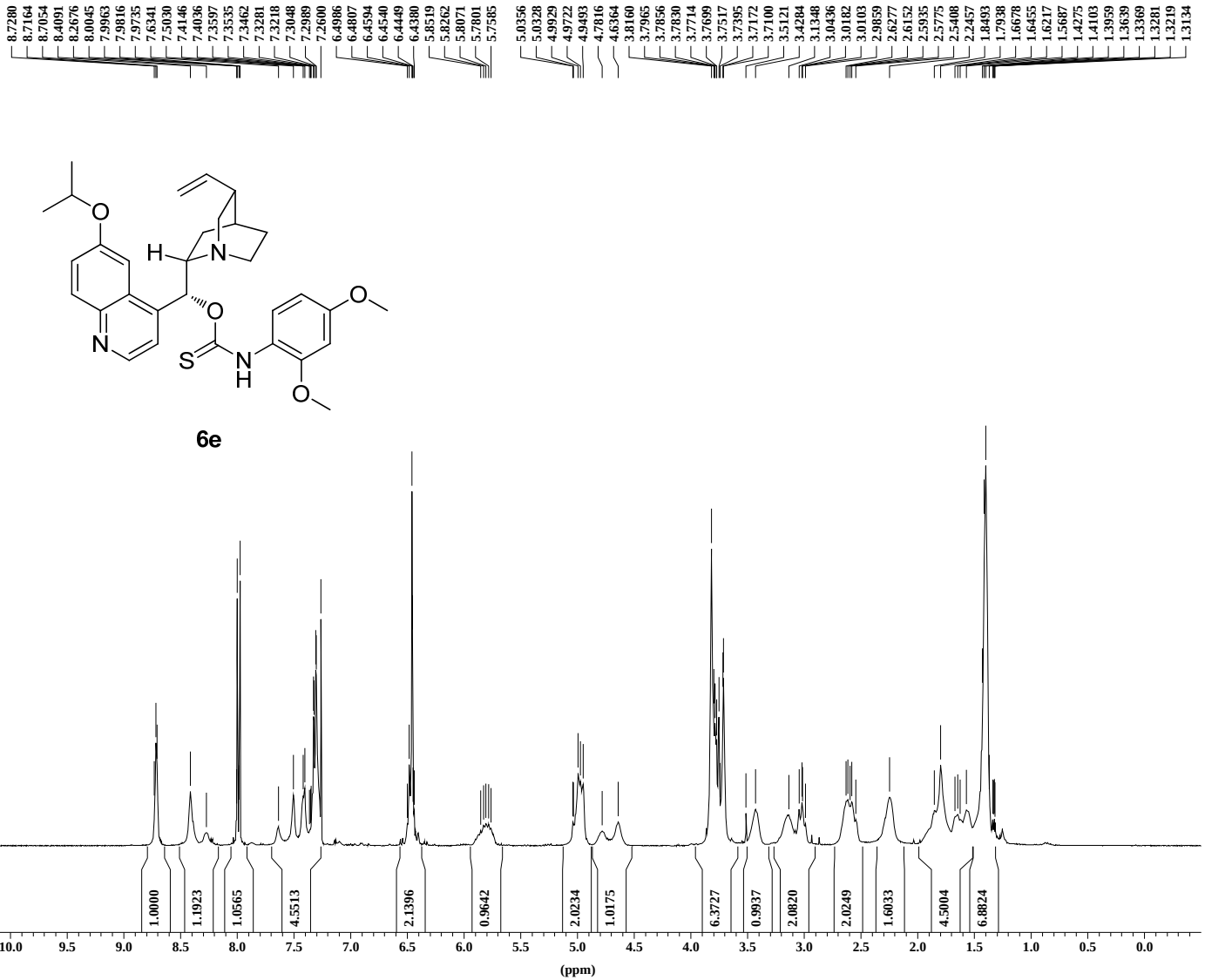





DT-030412-1-Ns-3-Ph-piperidine/2
1H
N
Ns
11
f1 (ppm)


DT-030412-1-Ns-3-Ph-piperidine/3
13C
N
Ns
11
150.131
142.513
141.974
128.722
127.191
127.096
124.327
77.212
76.788
52.586
46.397
42.169
30.305
25.039
f1 (ppm)

2,4-(OMe)2-isoprop



***** Current Data Parameters *****

NAME	:	dec23zl
EXPNO	:	3
PROCNO	:	1

***** Acquisition Parameters *****

LOCNUC	:	2H
NS	:	8
NUCLEUS	:	off
O1	:	2470.97 Hz
PULPROG	:	zg30
SFO1	:	400.1324710 MHz
SOLVENT	:	CDCl3
SW	:	20.5524 ppm
TD	:	65536
TE	:	299.4 K

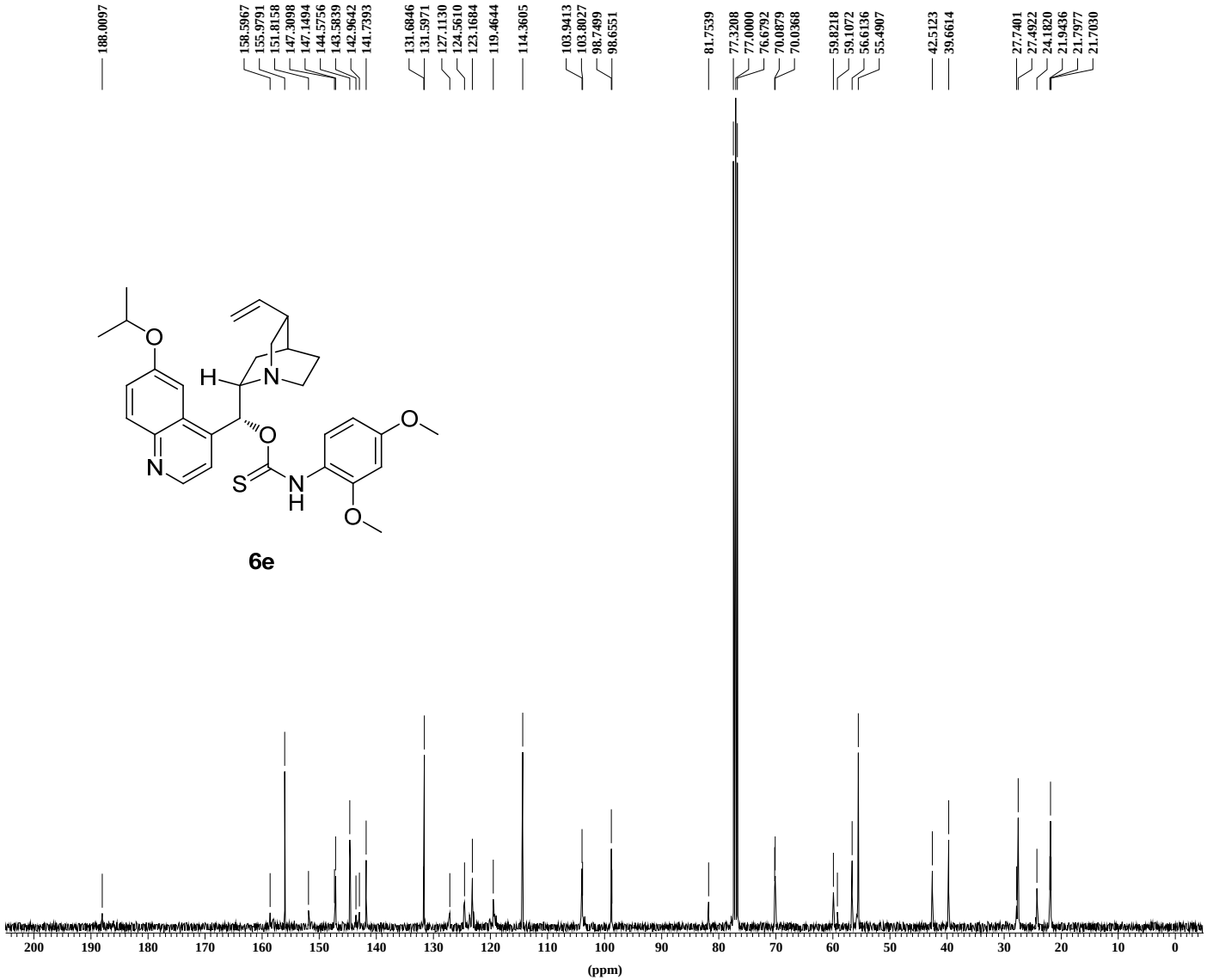
***** Processing Parameters *****

LB	:	0.30 Hz
SF	:	400.1300100 MHz

***** 1D NMR Plot Parameters *****

NUCLEUS	:	off

2,4-(OMe)2-isoprop



6e

***** Current Data Parameters *****

NAME	:	dec23zl
EXPNO	:	4
PROCNO	:	1

***** Acquisition Parameters *****

LOCNUC	:	2H
NS	:	1024
NUCLEUS	:	off
O1	:	11067.40 Hz
PULPROG	:	zgpg30
SFO1	:	100.6238364 MHz
SOLVENT	:	CDCl3
SW	:	238.8943 ppm
TD	:	65536
TE	:	299.9 K

***** Processing Parameters *****

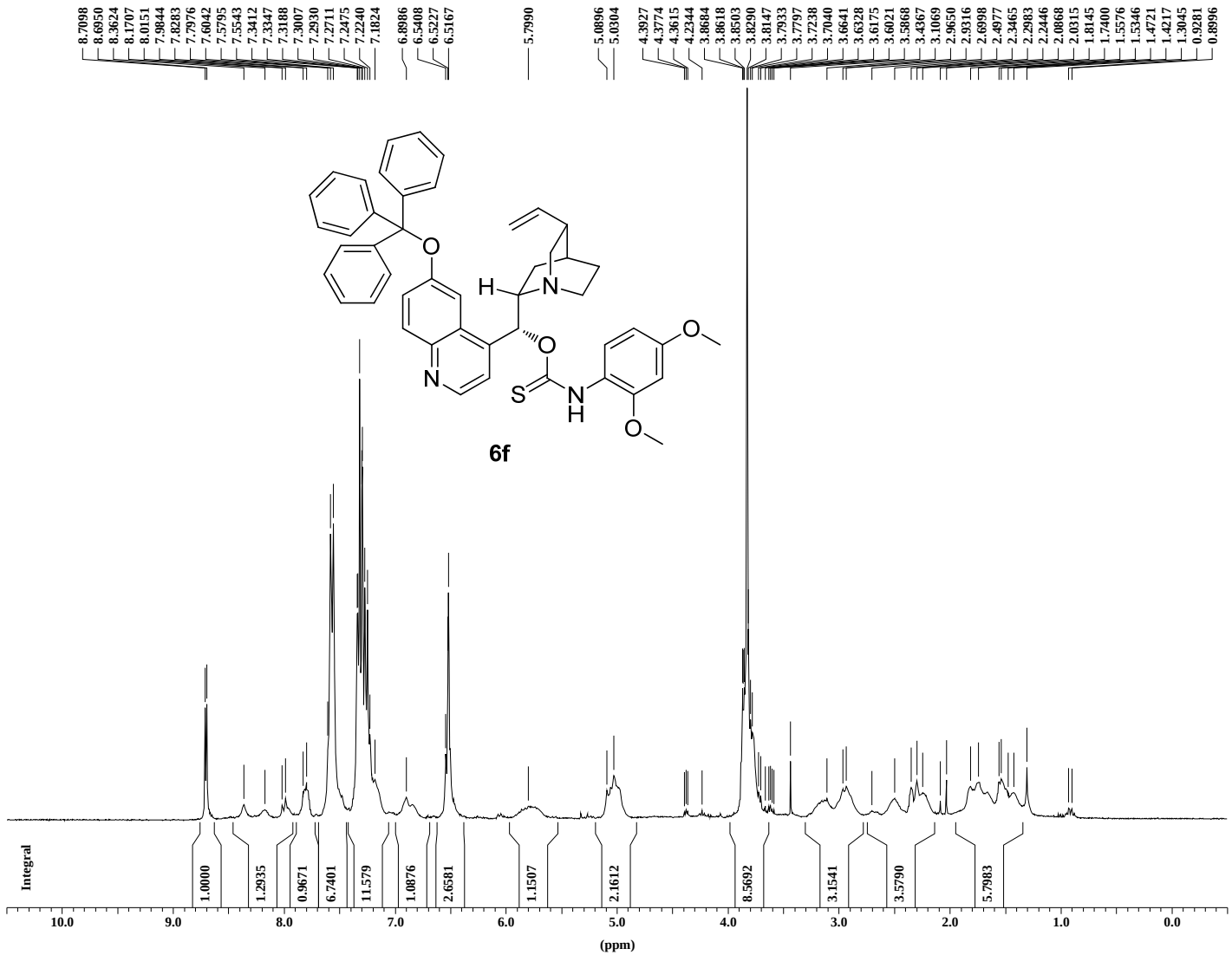
LB	:	1.00 Hz
SF	:	100.6127760 MHz

***** 1D NMR Plot Parameters *****

NUCLEUS	:	off

1H normal range AC300

CPh3



*** Current Data Parameters ***

NAME : de24zl

EXPNO : 1

PROCNO : 1

*** Acquisition Parameters ***

LOCNUC : 2H

NS : 8

NUCLEUS : off

O1 : 1853.43 Hz

PULPROG : zg30

SFO1 : 300.1318534 MHz

SOLVENT : CDCl3

SW : 17.9519 ppm

TD : 32768

TE : 679.5 K

*** Processing Parameters ***

LB : 0.30 Hz

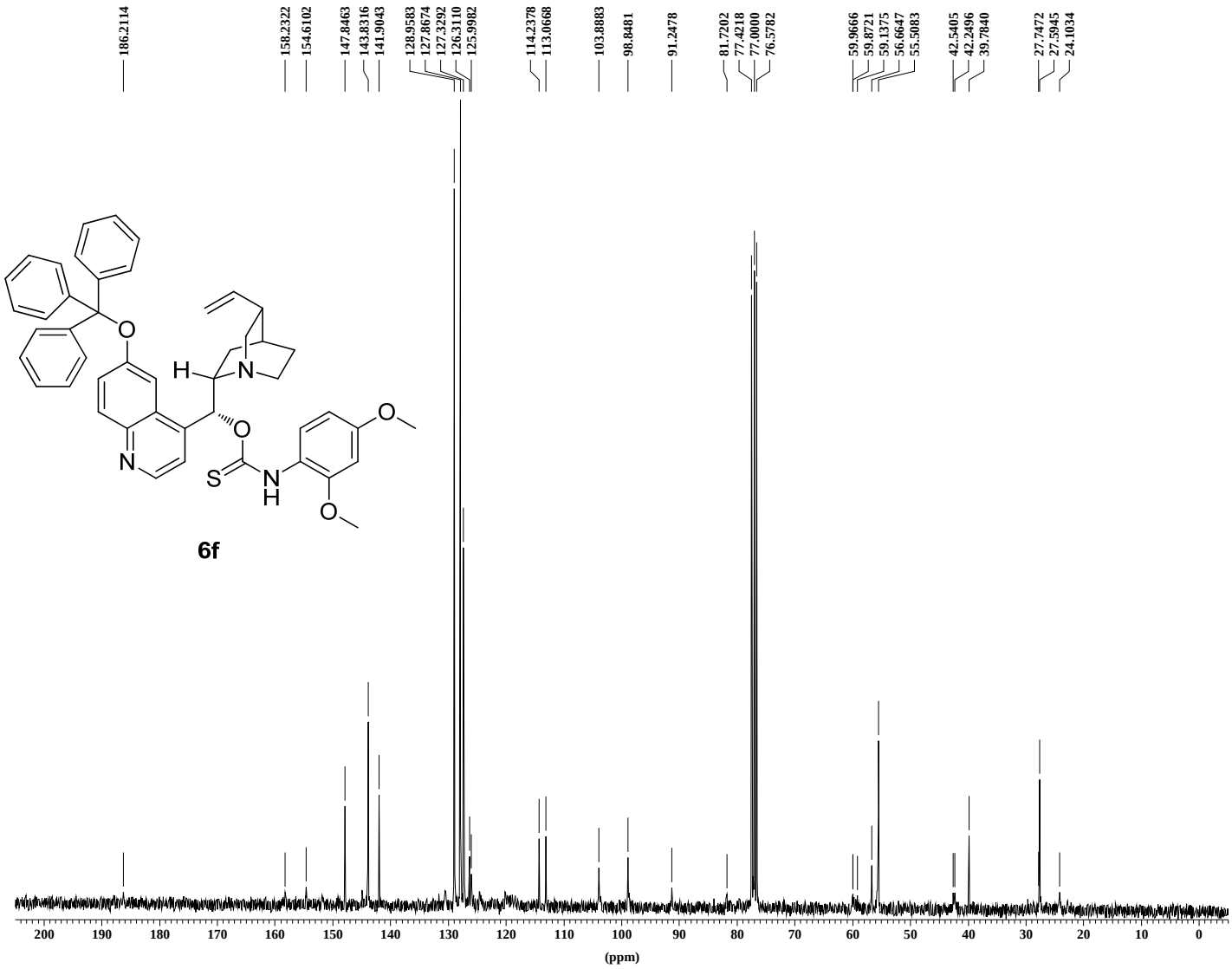
SF : 300.1300000 MHz

*** 1D NMR Plot Parameters ***

NUCLEUS : off

13C Standard AC300

CPh3



6f

***** Current Data Parameters *****

NAME	:	de24zl
EXPNO	:	2
PROCNO	:	1

***** Acquisition Parameters *****

LOCNUC	:	2H
NS	:	2599
NUCLEUS	:	off
O1	:	7924.11 Hz
PULPROG	:	zgpg30
SFO1	:	75.4756731 MHz
SOLVENT	:	CDCl3
SW	:	238.2968 ppm
TD	:	32768
TE	:	679.5 K

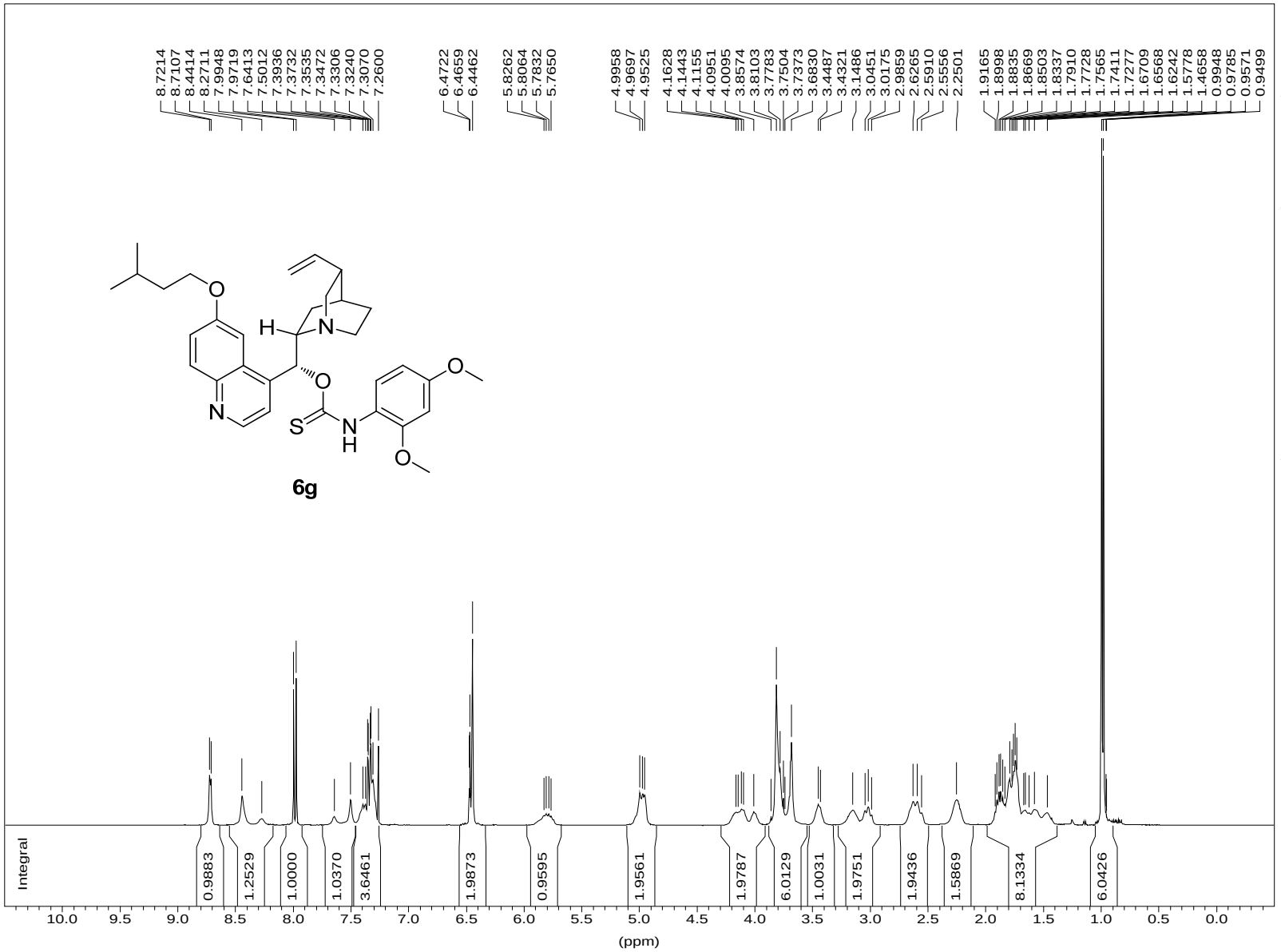
***** Processing Parameters *****

LB	:	1.00 Hz
SF	:	75.4677540 MHz

***** 1D NMR Plot Parameters *****

NUCLEUS	:	off

2,4-(OMe)2-bigtail



*** Current Data Parameters ***

NAME	:	dec23zl
EXPNO	:	1
PROCNO	:	1

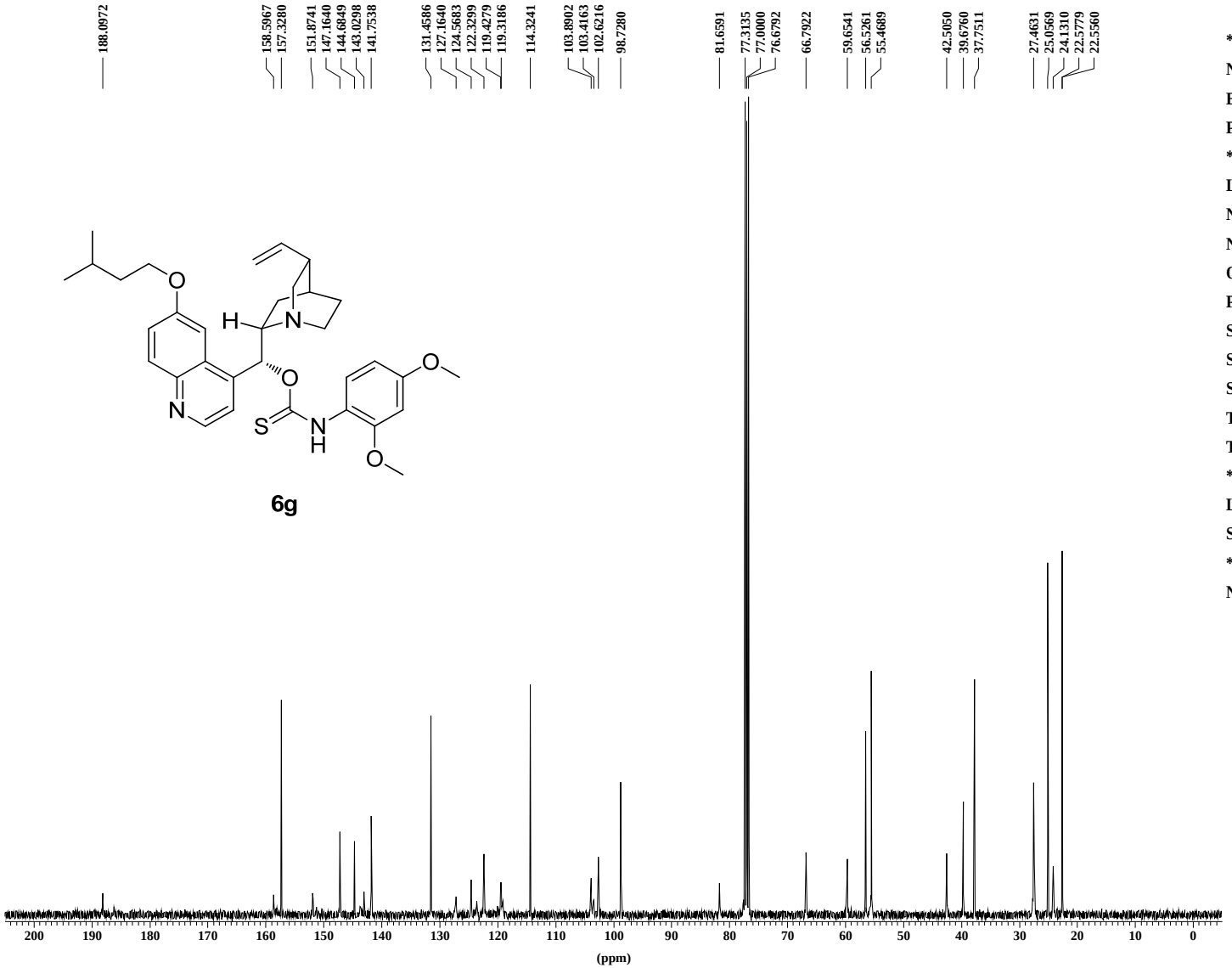
*** Acquisition Parameters ***

BF1	:	400.1300000 MHz
LOCNUC	:	2H
NS	:	8
O1	:	2470.97 Hz
PULPROG	:	zg30
SFO1	:	400.1324710 MHz
SOLVENT	:	CDCl3
SW	:	20.5524 ppm

*** Processing Parameters ***

LB	:	0.30 Hz
PHC0	:	-48.365 degree
PHC1	:	-16.793 degree

2,4-(OMe)2-bigtail



*** Current Data Parameters ***

NAME : dec23zl

EXPNO : 2

PROCNO : 1

*** Acquisition Parameters ***

LOCNUC : 2H

NS : 1024

NUCLEUS : off

O1 : 11067.40 Hz

PULPROG : zgpg30

SFO1 : 100.6238364 MHz

SOLVENT : CDCl3

SW : 238.8943 ppm

TD : 65536

TE : 299.9 K

*** Processing Parameters ***

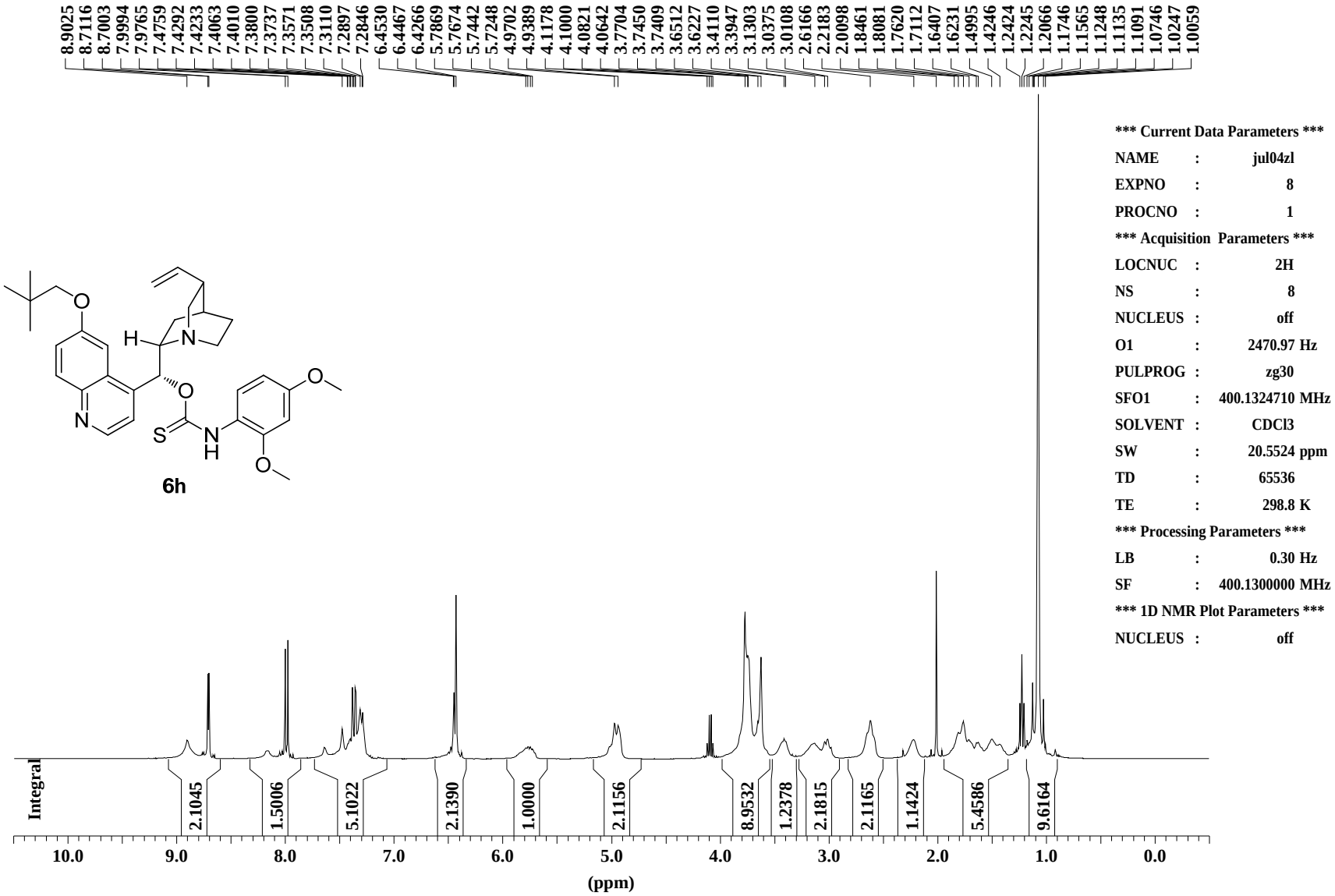
LB : 1.00 Hz

SF : 100.6127770 MHz

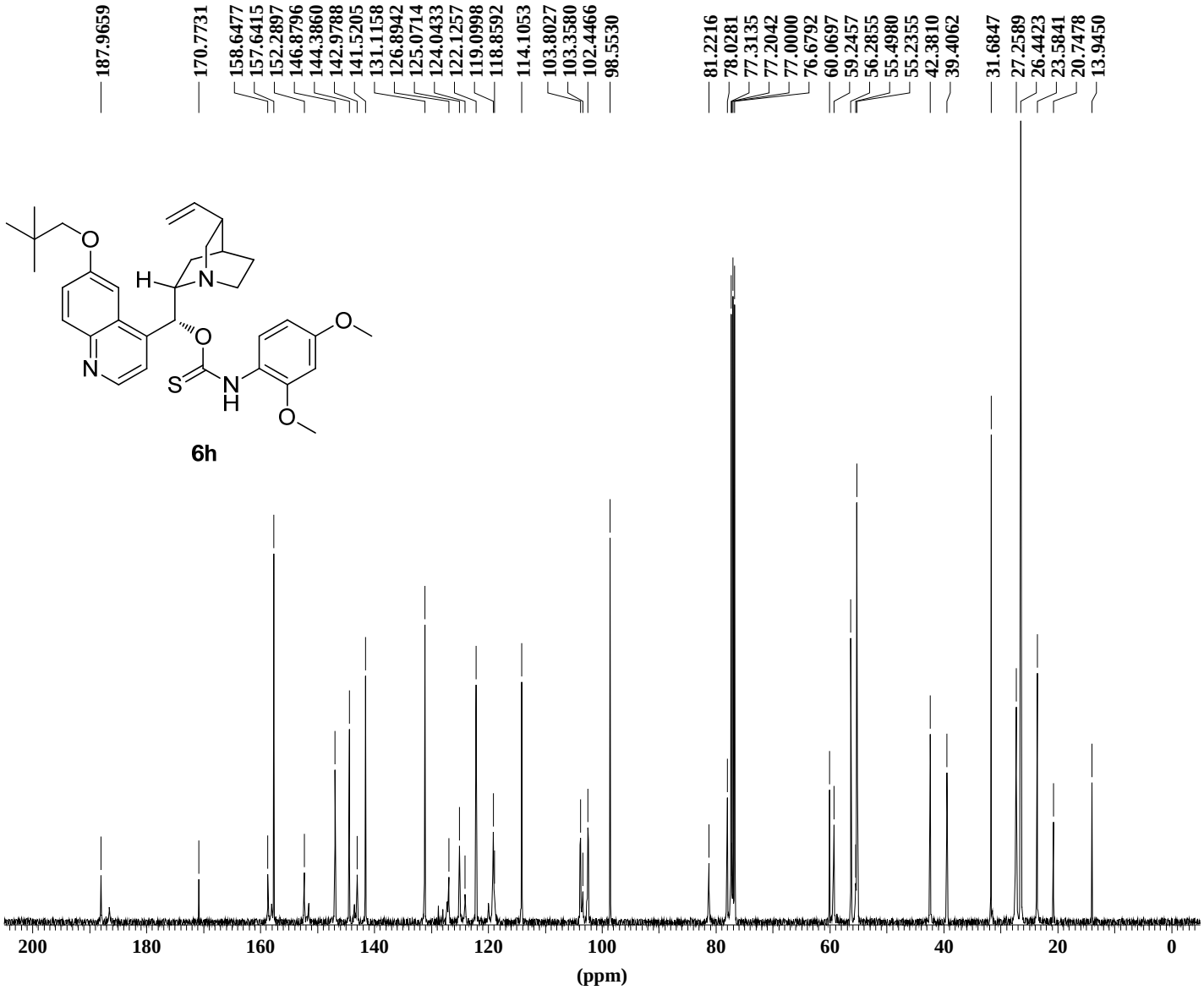
*** 1D NMR Plot Parameters ***

NUCLEUS : off

171A


8.9025
8.7116
8.7003
7.9994
7.9765
7.4759
7.4292
7.4233
7.4063
7.4010
7.3800
7.3737
7.3571
7.3508
7.3110
7.2897
7.2846
6.4530
6.4467
6.4266
5.7869
5.7674
5.7442
5.7248
4.9702
4.9389
4.1178
4.1000
4.0821
4.0642
3.7704
3.7450
3.7409
3.6512
3.6227
3.4110
3.3947
3.1303
3.0375
3.0108
2.6166
2.2183
2.0098
1.8461
1.8081
1.7620
1.7112
1.6407
1.6231
1.4995
1.4246
1.2424
1.2245
1.2066
1.1746
1.1565
1.1248
1.1135
1.1091
1.0746
1.0247
1.0059
6h
*** Current Data Parameters ***
NAME : jul04zl
EXPNO : 8
PROCNO : 1
*** Acquisition Parameters ***
LOCNUC : 2H
NS : 8
NUCLEUS : off
O1 : 2470.97 Hz
PULPROG : zg30
SFO1 : 400.1324710 MHz
SOLVENT : CDCl3
SW : 20.5524 ppm
TD : 65536
TE : 298.8 K
*** Processing Parameters ***
LB : 0.30 Hz
SF : 400.1300000 MHz
*** 1D NMR Plot Parameters ***
NUCLEUS : off
Integral
2.1045
1.5006
5.1022
2.1390
1.0000
2.1156
8.9532
1.2378
2.1815
2.1165
1.1424
5.4586
9.6164
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

171A



*** Current Data Parameters ***

NAME	:	jul04zl
EXPNO	:	9
PROCNO	:	1

*** Acquisition Parameters ***

LOCNUC	:	2H
NS	:	1024
NUCLEUS	:	off
O1	:	11067.40 Hz
PULPROG	:	zgpg30
SFO1	:	100.6238364 MHz
SOLVENT	:	CDCl3
SW	:	238.8943 ppm
TD	:	65536
TE	:	299.6 K

*** Processing Parameters ***

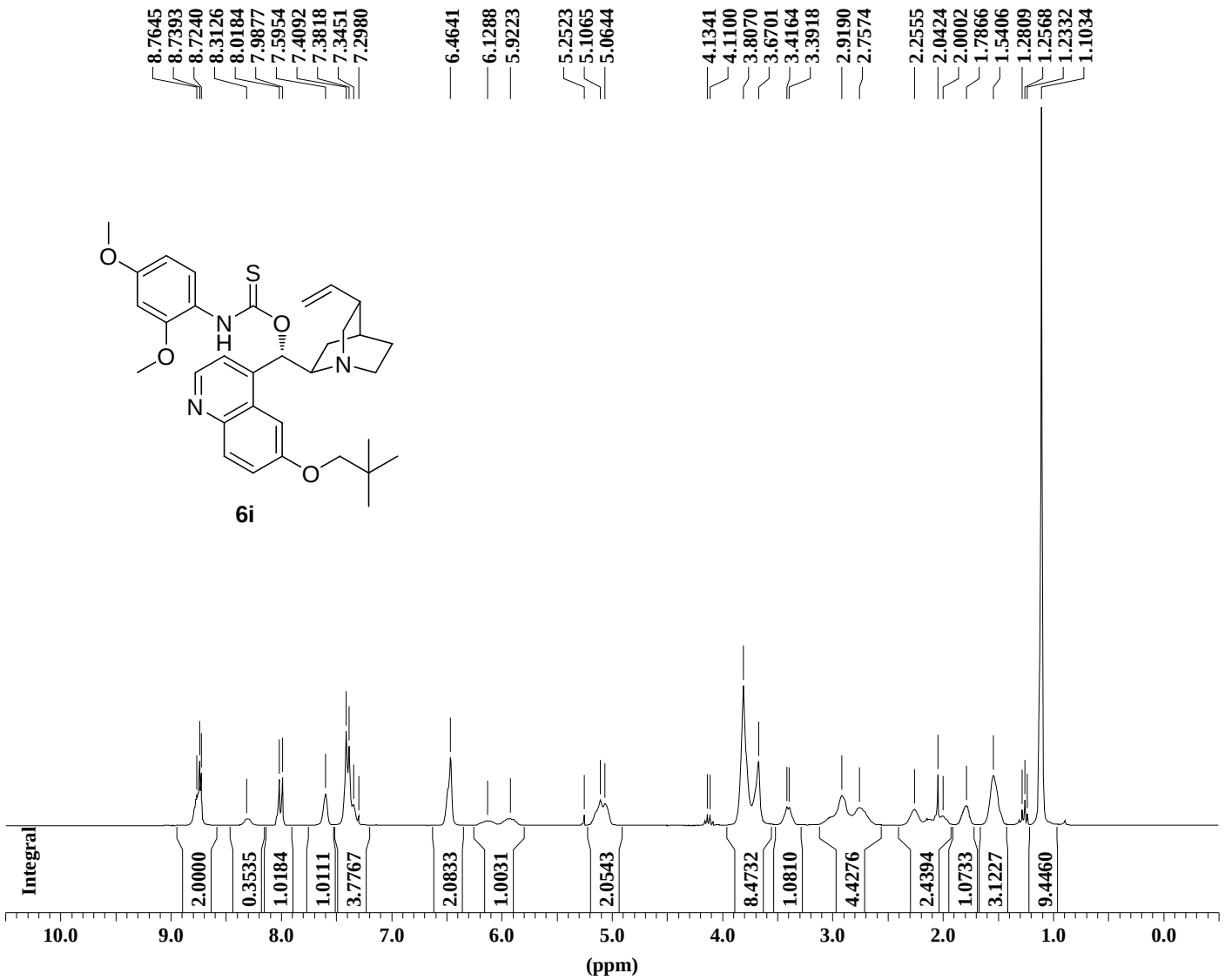
LB	:	1.00 Hz
SF	:	100.6127950 MHz

*** 1D NMR Plot Parameters ***

NUCLEUS	:	off

1H normal range AC300

3213D-QND



6i

***** Current Data Parameters *****

NAME	:	oc15zl
EXPNO	:	1
PROCNO	:	1

***** Acquisition Parameters *****

LOCNUC	:	2H
NS	:	8
NUCLEUS	:	off
O1	:	1853.43 Hz
PULPROG	:	zg30
SFO1	:	300.1318534 MHz
SOLVENT	:	CDCl3
SW	:	17.9519 ppm
TD	:	32768
TE	:	296.7 K

***** Processing Parameters *****

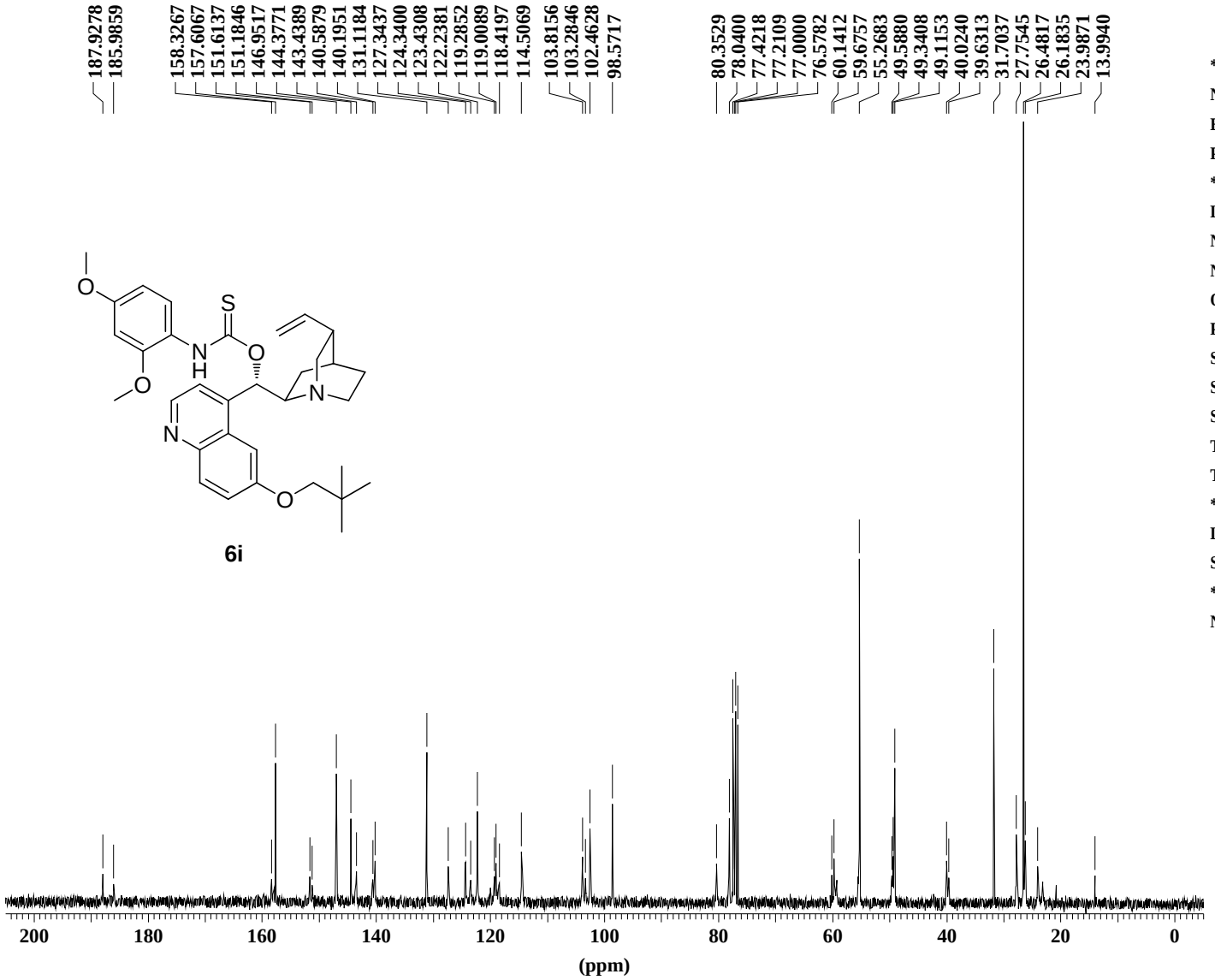
LB	:	0.30 Hz
SF	:	300.1300000 MHz

***** 1D NMR Plot Parameters *****

NUCLEUS	:	off

13C Standard AC300

3213D-QND-cat



6i

***** Current Data Parameters *****

NAME	:	oc15zl
EXPNO	:	2
PROCNO	:	1

***** Acquisition Parameters *****

LOCNUC	:	2H
NS	:	266
NUCLEUS	:	off
O1	:	7924.11 Hz
PULPROG	:	zgpg30
SFO1	:	75.4756731 MHz
SOLVENT	:	CDCl3
SW	:	238.2968 ppm
TD	:	32768
TE	:	296.9 K

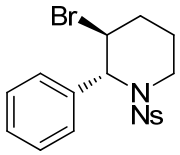
***** Processing Parameters *****

LB	:	1.00 Hz
SF	:	75.4677680 MHz

***** 1D NMR Plot Parameters *****

NUCLEUS	:	off

Figure S1. X-ray structure of **2a**.



2a

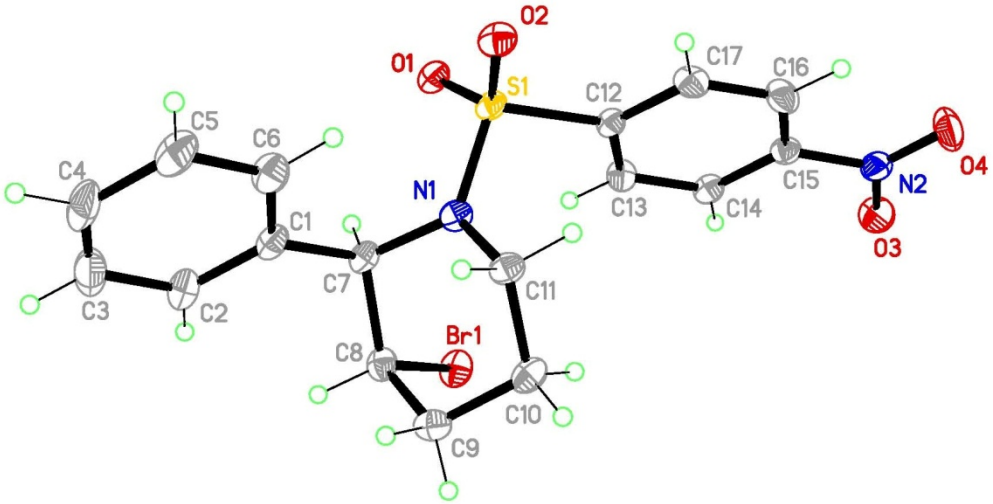
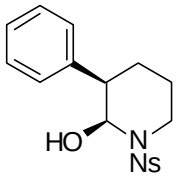


Figure S2. X-ray structure of **ent-3a**.



ent-3a