Supporting Information

Nickel-Catalyzed Hydrogenolysis and Conjugate Addition Of 2-Hydroxymethylpyridines via Organozinc Intermediates

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I. General Procedures

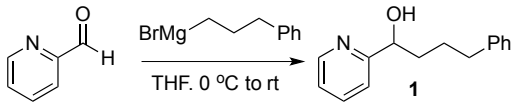
All reactions were carried out under an atmosphere of N_2, or Ar when noted. All glassware was oven- or flame-dried prior to use. Tetrahydrofuran (THF), diethyl ether (Et_2O), dichloromethane (CH_2Cl_2), and toluene (PhMe) were degassed with Ar and then passed through two 4 x 36 inch columns of anhydrous neutral A-2 alumina (8 x 14 mesh; LaRoche Chemicals; activated under a flow of argon at 350 ^oC for 12 h) to remove H_2O. All other solvents utilized were purchased "anhydrous" commercially, or purified as described. ^1H NMR spectra were recorded on Bruker DRX-400 (400 MHz ^1H, 100 MHz ^{13}C, 376.5 MHz ^{19}F), GN-500 (500 MHz ^1H, 125.7 MHz ^{13}C), or CRYO-500 (500 MHz ^1H, 125.7 MHz ^{13}C) spectrometers. Proton chemical shifts are reported in ppm (δ) relative to internal tetramethylsilane (TMS, δ 0.00). Data are reported as follows: chemical shift (multiplicity [singlet (s), broad singlet (br s), doublet (d), doublet of doublets (dd), triplet (t), doublet of triplets (dt), doublet of doublet of triplets (ddt), triplet of triplets (tt), quartet (q), quintet (quin), apparent doublet (ad), apparent triplet (at), multiplet (m)], coupling constants [Hz], integration). Carbon chemical shifts are reported in ppm (δ) relative to TMS with the respective solvent resonance as the internal standard ($CDCl_3$, δ 77.16 ppm). Unless otherwise indicated, NMR data were collected at 25 ^oC. Infrared (IR) spectra were obtained on a Thermo Scientific Nicolet iS5 spectrometer with an iD5 ATR tip (neat) and are reported in terms of frequency of absorption (cm^{-1}). Analytical thin-layer chromatography (TLC) was performed using Silica Gel 60 F_{254} precoated plates (0.25 mm thickness). Visualization was accomplished by irradiation with a UV lamp and/or staining with $KMnO_4$, ceric ammonium molybdate (CAM), or *p*-anisaldehyde (PAA) solutions. Flash chromatography was performed using Silica Gel 60 (170-400 mesh) from Fisher Scientific. Melting points (m.p.) were obtained using a Mel-Temp melting point apparatus and are uncorrected. High resolution mass spectrometry was performed by the University of California, Irvine Mass Spectrometry Center.

[1,2-Bis(diphenylphosphino)ethane]dichloronickel(II) was purchased from Strem, stored in a glovebox under an atmosphere of N_2, and used as received. Diethylzinc ($ZnEt_2$) and diethyl chlorophosphate were purchased from Sigma and used as received. 1-isoquinolinecarboxaldehyde was prepared from selenium (IV) oxide oxidation of 1-methylisoquinoline by a procedure reported by Long.[1] All other reagents were purchased commercially and used as received.

[1] Cao, B.; Wang, Y.; Ding, K.; Neamati, N.; Long, Y-Q. *Org. Biomol. Chem.* **2012**, *10*, 1239.

II. Synthesis and Characterization of Benzylic Alcohols

General Procedure A. *Grignard addition to aldehydes.*



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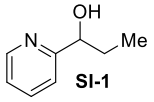
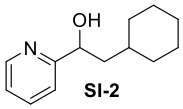
1. In a flame-dried round-bottom flask, a solution of 2-pyridinecarboxaldehyde (1.43 mL, 15.0 mmol, 1.00 equiv) in THF (30 mL) was cooled to 0 °C and 3-(phenylpropyl)magnesium bromide (1.6 M in THF, 10 mL, 16 mmol, 1.1 equiv) was added. The reaction mixture was stirred at room temperature for 1 h, then cooled to 0 °C and saturated ammonium chloride (25 mL) was added. The reaction was extracted with EtOAc (3 x 25 mL). The combined organic layers were washed with brine (1 x 40 mL), dried over Na_2SO_4, and concentrated in vacuo. The product was purified by column flash chromatography (25–40% EtOAc/hexanes) to afford the title compound as a yellow solid (1.70 g, 7.50 mmol, 50%). **TLC R_f** = 0.16 (20% EtOAc/hexanes, UV active); **m.p.** = 58–60 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.53 (d, *J* = 4.8 Hz, 1H), 7.66 (td, *J* = 7.8, 1.8 Hz, 1H), 7.29–7.23 (m, 2H), 7.22–7.13 (m, 5H), 4.75 (s, 1H), 4.19 (s, 1H), 2.71–2.59 (m, 2H), 1.91–1.82 (m, 1H), 1.80–1.67 (m, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 161.9, 148.2, 142.4, 136.7, 128.5, 128.3, 125.8, 122.3, 120.4, 72.5, 38.2, 35.8, 26.9; **IR** (neat) 3192, 2925, 2861, 1594, 1492, 1452 cm^{-1}; **HRMS** (TOF MS ES+) *m* / *z* calcd for $C_{15}H_{17}NONa$ $(M + Na)^+$ 227.1310, found 227.1315.



SI-1

SI-1. Prepared according to a procedure reported by Braga[2], the following amounts of reagents were used: 2-pyridinecarboxaldehyde (0.38 mL, 4.0 mmol, 1.0 equiv), ethylmagnesium bromide (2.4 M in Et_2O, 2.0 mL, 4.8 mmol, 1.2 equiv), and THF (15 mL). Analytical data is consistent with literature values.[3] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.55 (dt, *J* = 4.9, 1.3 Hz, 1H), 7.68 (td, *J* = 7.6, 1.8 Hz, 1H), 7.25 (dd, *J* = 7.8 Hz, 0.5 Hz, 1H), 7.20 (ddd, *J* = 7.6, 4.9, 0.5 Hz, 1H), 4.73–4.66 (m, 1H), 4.17 (d, *J* = 5.5 Hz, 1H), 1.95–1.84 (m, 1H), 1.78–1.66 (m, 1H), 0.95 (t, *J* = 7.3 Hz, 3H).

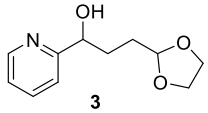


SI-2

SI-2. Using General Procedure A, outlined above, the following amounts of reagents were used: 2-pyridinecarboxaldehyde (0.48 mL, 5.0 mmol, 1.0 equiv), (cyclohexylmethyl)magnesium bromide (0.56 M in THF, 9.8 mL, 11 mmol, 1.1 equiv), and THF (10 mL). The product was purified by column flash chromatography (20% EtOAc/hexanes) to afford the title compound as a yellow solid (0.453 g, 2.20 mmol, 44%). **TLC R_f** = 0.3 (20% EtOAc/hexanes, UV active); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.51 (d, *J* = 4.7 Hz, 1H), 7.66 (t, *J* = 7.7 Hz, 1H), 7.26 (d, *J* = 7.7 Hz, 1H), 7.19 (t, *J* = 6.0 Hz, 1H), 4.82 (t, *J* = 6.3, 1H), 4.28 (br s, 1H), 1.94 (d, *J* = 12.7 Hz, 1H), 1.75–1.54 (m, 7H) 1.32–1.11 (m, 3H), 1.02–0.90 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 163.4, 148.3, 136.7, 122.2,

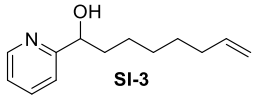
[2] Braga, A. L.; Paixao, M. W.; Ludtke, D. S.; Silveira, C. C.; Rodrigues, O. E. D. *Org. Lett.* **2003**, *5*, 2365.
[3] Moody, C. J.; Morfitt, C. N. *Synthesis* **1998**, *7*, 1039.

120.4, 70.7, 46.9, 34.4, 34.2, 32.7, 26.7, 26.5, 26.2; **IR** (neat) 3217, 2919, 1594 cm^{-1}; **HRMS** (TOF MS ES+) *m* / *z* calcd for $C_{13}H_{19}NONa$ $(M + Na)^+$ 228.1364, found 228.1364.



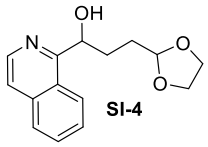
3

3. Using General Procedure A, outlined above, the following amounts of reagents were used: 2-pyridinecarboxaldehyde (0.95 mL, 10 mmol, 1.0 equiv), hept-6-en-1-ylmagnesium bromide (1.2 M in THF, 9.2 mL, 11 mmol, 1.1 equiv), and THF (10 mL). The product was purified by column flash chromatography (25–40% EtOAc/hexanes) to afford the title compound as a yellow oil (1.31 g, 6.38 mmol, 64%). Analytical data is consistent with literature values.[4] **TLC R_f** = 0.1 (50% EtOAc/hexanes, UV active); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.55–8.50 (m, 1H), 7.67 (td, *J* = 7.8, 1.8 Hz, 1H), 7.29 (d, *J* = 7.8 Hz, 1H), 7.21–7.15 (m, 1H), 4.93–4.88 (m, 1H), 4.83–4.75 (m, 1H), 4.33 (d, *J* = 5.4 Hz, 1H), 3.99–3.80 (m, 4H), 2.07–1.95 (m, 1H), 1.87–1.74 (m, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 161.9, 148.3, 136.7, 122.3, 120.4, 104.4, 72.4, 64.9, 32.5, 29.5.



SI-3

SI-3. Using General Procedure A, outlined above, the following amounts of reagents were used: 2-pyridinecarboxaldehyde (0.95 mL, 10 mmol, 1.0 equiv), hept-6-en-1-ylmagnesium bromide (1.2 M in THF, 9.2 mL, 11 mmol, 1.1 equiv), and THF (10 mL). The product was purified by column flash chromatography (25–40% EtOAc/hexanes) to afford the title compound as a red oil (1.31 g, 6.38 mmol, 64%). **TLC R_f** = 0.4 (40% EtOAc/hexanes, UV active); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.53 (d, *J* = 4.7 Hz 1H), 7.67 (t, *J* = 7.6 Hz, 1H), 7.26 (d, *J* = 7.6 Hz, 1H), 7.19 (t, *J* = 5.5 Hz, 1H), 5.79 (ddt, *J* = 17.2, 10.2, 6.9 Hz, 1H), 4.98 (d, *J* = 17.2 Hz, 1H), 4.92 (d, *J* = 10.2 Hz, 1H), 4.73 (dd, *J* = 7.7, 4.4 Hz, 1H), 4.25 (br s, 1H), 2.03 (dd, *J* = 10.2, 6.9 Hz, 2H), 1.87–1.77 (m, 1H) 1.74–1.65 (m, 1H), 1.50–1.24 (m, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.4, 148.3, 139.2, 136.7, 122.3, 120.4, 114.3, 72.9, 38.7, 33.8, 29.2, 28.9, 25.2; **IR** (neat) 3260, 2926, 1594 cm^{-1}; **HRMS** (TOF MS ES+) *m* / *z* calcd for $C_{13}H_{19}ONNa$ $(M + Na)^+$ 228.1364, found 228.1364.



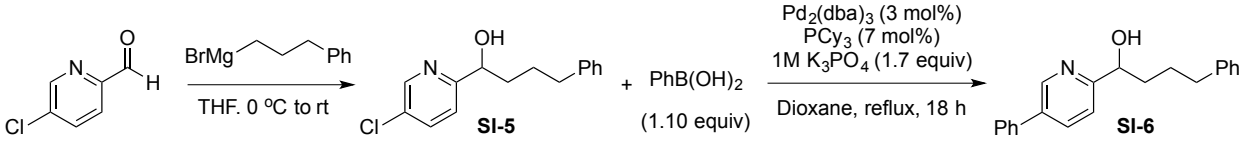
SI-4

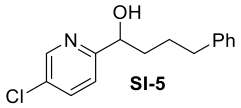
SI-4. Using General Procedure A, outlined above, the following amounts of reagents were used: 1-Isoquinolinecarboxaldehyde (0.47 g, 3.0 mmol, 1.0 equiv), (2-(1,3-dioxolan-2-yl)ethyl)magnesium bromide (0.95 M in THF, 3.5 mL, 3.3 mmol, 1.1 equiv), and THF (10 mL). The product was purified by column flash chromatography (40% EtOAc/hexanes) to afford the title compound as a tan solid (249 mg, 0.960 mmol, 32%). **TLC R_f** = 0.2 (40% EtOAc/hexanes, UV active); **m.p.** = 53–55 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.43 (d, *J* = 5.8 Hz, 1H), 8.07 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 8.4 Hz, 1H), 7.69 (t, *J* = 7.7 Hz, 1H), 7.61 (t, *J* = 7.7 Hz, 1H), 7.58 (d, *J* = 5.8 Hz, 1H), 5.52 (d, *J* = 7.1 Hz, 1H), 5.18 (br s, 1H), 4.93 (t, *J* = 4.8 Hz, 1H), 4.00–3.89 (m, 2H), 3.87–3.78

[4] Gebert, A.; Barth, M.; Linden, A.; Widmer, U.; Heimgartner, H. *Helv. Chim. Acta* **2012**, *95*, 737.

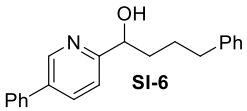
(m, 2H) 2.12–2.02 (m, 1H), 2.06–1.97 (m, 1H), 1.90–1.81 (m, 1H), 1.80–1.72 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 161.1, 140.4, 136.5, 130.3, 126.6, 126.5, 124.9, 124.4, 120.6, 104.5, 69.2, 65.0, 64.9, 33.3, 29.6; **IR** (neat) 3390, 2957, 2882 cm^{-1}; **HRMS** (TOF MS ES+) *m* / *z* calcd for $C_{15}H_{17}O_3NNa$ $(M + Na)^+$ 282.1106, found 282.1104.

i. Synthesis of Alcohol Precursor of 11 (Scheme 3)





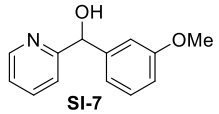
SI-5. Using General Procedure A, outlined above, the following amounts of reagents were used: 5-chloro-2-formylpyridine (0.85 g, 6.0 mmol, 1.0 equiv), (3-phenylpropyl)magnesium bromide (1.6 M in THF, 4.1 mL, 6.6 mmol, 1.1 equiv), and THF (20 mL). The product was purified by column flash chromatography (20% EtOAc/hexanes) to afford the title compound as a red oil (0.88 g, 3.4 mmol, 56%). **TLC R_f** = 0.3 (20% EtOAc/hexanes, UV active); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.47 (d, *J* = 1.7 Hz, 1H), 7.62 (dd, *J* = 8.4, 2.3 Hz, 1H), 7.26 (t, *J* = 7.5 Hz, 2H), 7.21–7.12 (m, 4H), 4.76–4.71 (m, 1H), 3.80 (br s, 1H), 2.72–2.58 (m, 2H), 1.87–1.78 (m, 1H), 1.77–1.68 (m, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 160.6, 147.3, 142.2, 136.6, 130.6, 128.5, 128.4, 125.9, 121.2, 72.7, 38.0, 35.8, 27.0; **IR** (neat) 3359, 2936, 2859 cm^{-1}; **HRMS** (TOF MS ES+) *m* / *z* calcd for $C_{15}H_{16}ClNONa$ $(M + Na)^+$ 284.0818, found 284.0810.



SI-6. The product was prepared according to a modified procedure by Fu.[5] Tris(dibenzylideneacetone)dipalladium (69 mg, 0.076 mmol, 3 mol %) and tricyclohexylphosphine (50 mg, 0.18 mmol, 7 mol %) were charged into a flame round bottom flask inside a glovebox. The flask was fitted with a septum, removed from the glovebox, and phenylboronic acid (0.337 g, 2.77 mmol, 1.10 equiv), **4.22** (0.66 g, 2.5 mmol, 1.0 equiv), aqueous potassium phosphate (1.3 M in H_2O, 3.3 mL, 4.3 mmol, 1.7 equiv) and dioxane (13 mL) were added. The reaction flask was fitted with a reflux condenser and heated to 95 °C for 18 h. After cooling, the solvent was removed under reduced pressure. The resultant residue was purified by flash column chromatography (30% EtOAc/hexane) to afford the title compound as a pale yellow solid (0.488 g, 1.60 mmol, 64%). **TLC R_f** = 0.4 (40% EtOAc/hexanes, UV active); **m.p.** = 99–101 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.75 (d, *J* = 2.0 Hz, 1H), 7.85 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.57 (d, *J* = 7.2 Hz, 2H), 7.48 (t, *J* = 7.2 Hz, 2H), 7.40 (t, *J* = 7.2 Hz, 1H), 7.31–7.23 (m, 3H), 7.21–7.14 (m, 3H), 7.85 (m, 1H), 4.15 (d, *J* = 5.1 Hz, 1H), 2.73–2.61 (m, 2H), 1.96–1.86 (m, 1H), 1.84–1.73 (m, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 161.0, 146.7, 142.4, 137.7, 135.5, 135.3, 129.2,

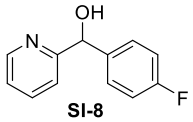
[5] Kudo, N.; Perseghini, M.; Fu, G. C. *Angew. Chem. Int. Ed.* **2006**, *45*, 1282.

128.6, 128.4, 128.2, 127.2, 125.8, 120.3, 72.6, 38.2, 35.9, 27.1; **IR** (neat) 3286, 2946, 2914 cm^{-1}; **HRMS** (TOF MS ES+) *m* / *z* calcd for $C_{21}H_{21}NONa$ $(M + Na)^+$ 326.1521, found 326.1516.



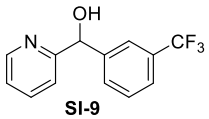
SI-7

SI-7. Using General Procedure A, outlined above, the following amounts of reagents were used: 2-pyridinecarboxaldehyde (0.95 mL, 10 mmol, 1.0 equiv), (3-methoxyphenyl)magnesium bromide (0.92 M in THF, 13 ml, 12 mmol, 1.2 equiv), and THF (20 mL). The product was purified by column flash chromatography (20–40% EtOAc/hexanes) to afford the title compound as a yellow oil (0.62 g, 3.1 mmol, 62%). Analytical data is consistent with literature values.[6] **TLC R_f** = 0.2 (20% EtOAc/hexanes, UV active); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.56 (d, *J* = 4.4 Hz, 1H), 7.62 (td, *J* = 7.5, 1.3 Hz, 1H), 7.29–7.14 (m, 3H), 6.96 (d, *J* = 6.7 Hz, 1H), 6.93 (s, 1H), 6.81 (d, *J* = 7.2 Hz, 1H), 5.27 (d, *J* = 3.6 Hz, 1H), 5.29 (d, *J* = 4.3 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 160.6, 159.8, 147.8, 144.8, 136.9, 129.6, 122.5, 121.4, 119.5, 113.5, 112.5, 74.9, 55.3.



SI-8

SI-8. Using General Procedure A, outlined above, the following amounts of reagents were used: 2-pyridinecarboxaldehyde (0.36 mL, 3.8 mmol, 1.1 equiv), (4-fluorophenyl)magnesium bromide (0.27 M in THF, 15 ml, 4.0 mmol, 1.2 equiv), and THF (20 mL). The product was purified by column flash chromatography (20–40% EtOAc/hexanes) to afford the title compound as a yellow oil (0.60 g, 3.0 mmol, 78%). Analytical data is consistent with literature values.[6] **TLC R_f** = 0.2 (20% EtOAc/hexanes, UV active); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.56 (d, *J* = 4.7 Hz, 1H), 7.62 (dt, *J* = 7.7, 1.8 Hz, 1H), 7.36–7.30 (m, 2H), 7.23–7.17 (m, 1H), 7.11 (d, *J* = 7.9 Hz, 1H), 7.05–6.97 (m, 2H), 5.73 (s, 1H), 5.31 (s, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 163.4 (d, J_{CF} = 245.0 Hz) 160.6, 147.9, 139.1 (d, J_{CF} = 2.77 Hz), 137.0, 128.9 (d, J_{CF} = 8.3 Hz), 122.6 (d, J_{CF} = 161.8 Hz), 115.6 (d, J_{CF} = 21.5 Hz), 74.31.



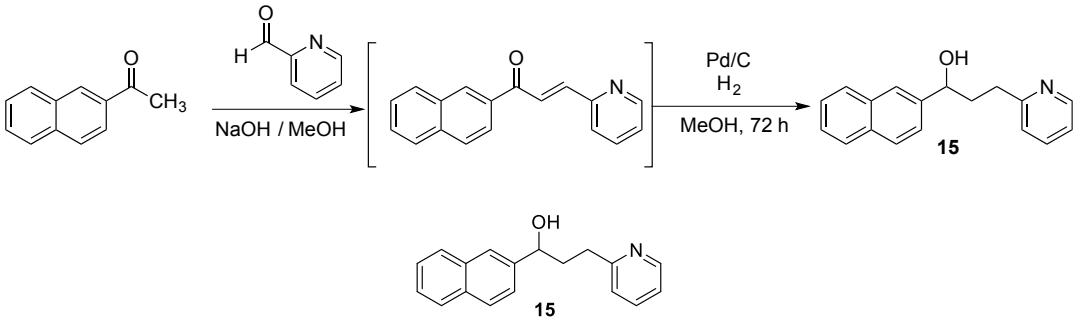
SI-9

SI-9. Using General Procedure A, outlined above, the following amounts of reagents were used: 2-pyridinecarboxaldehyde (0.95 mL, 10 mmol, 1.0 equiv), (3-(trifluoromethyl)phenyl)magnesium bromide (0.50 M in THF, 20 ml, 10 mmol, 1.2 equiv), and THF (20 mL). The product was purified by column flash chromatography (20–40% EtOAc/hexanes) to afford the title compound as a yellow oil (0.60 g, 3.0 mmol, 78%). Analytical data is consistent with literature values.[7] **TLC R_f** = 0.2 (20% EtOAc/hexanes, UV active); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.57 (d, *J* = 5.0 Hz, 1H), 7.69–7.62 (m, 2H), 7.57 (d, *J* = 7.8 Hz, 1H), 7.53 (d, *J* = 7.6 Hz, 1H), 7.45 (t, *J* = 8.0 Hz, 1H), 7.25–7.20 (m, 1H), 7.14 (d, *J* = 8.0 Hz, 1H), 5.80 (s, 1H), 5.44

[6] Kamitani, M.; Ito, M.; Itazaki, M.; Nakazawa, H. *Chem.Commun.* **2014**, *50*, 7941.
[7] Agai, B.; Proszenyak, A.; Tarkanyi, G.; Vida, L.; Faigl, F. *Eur. J. Org. Chem.* **2004**, 3623.

(s, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 159.9, 148.0, 144.2, 137.1, 130.8 (q *J* = 32.4 Hz), 130.4, 129.0, 124.7 (q, *J* = 4.16 Hz), 124.0 (q, *J* = 270 Hz), 123.8 (q, *J* = 3.70 Hz), 122.8, 121.2, 74.4.

ii. Synthesis of Substrate 15 for Scheme 4



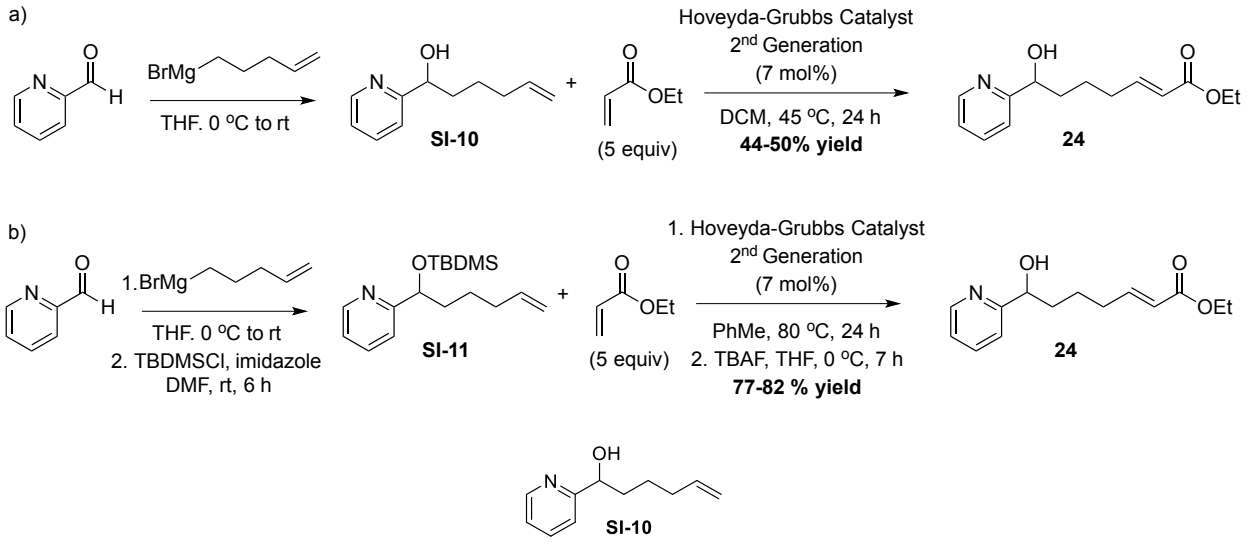
15. The product was prepared according to modified procedures by Attar[8] and Hirota.[9] To a 100 mL round bottomed flask equipped with a stir bar was added 2-acetonaphthone (6.81 g, 40.0 mmol, 1.00 equiv), MeOH (10 mL), and 10% NaOH (20 mL). The mixture was stirred for 15 min at room temperature before addition of 2-pyridinecarboxaldehyde (6.85 mL, 72.0 mmol, 1.80 equiv). The reaction was stirred until judged complete by TLC analysis (2 h). Ice water was added to the reaction and the solid was filtered, washed with Et_2O, and dried in vacuo. The unpurified solid enone was then redissolved in MeOH (40 mL) and transferred to a round bottom flask containing a stir bar and 10% Pd/C (0.68 g, 10% by weight relative to 2-acetonaphthone). The flask was flushed with nitrogen and then equipped with a balloon of hydrogen gas. The reaction was stirred under an atmosphere of hydrogen for 72 h. The reaction mixture was flushed with N_2, then filtered through celite, washing with MeOH. The filtrate was poured into sat. aqueous $NaHCO_3$ (60 mL) and extracted with EtOAc (3 x 50 mL). The combined organics were washed with brine, dried with Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by flash column chromatography (10–30% EtOAc/hexanes) to afford alcohol **15** as a white solid (1.63 g, 6.20 mmol, 16%). **TLC R_f** = 0.2 (20% EtOAc/hexanes, UV active); **m.p.** = 76–77 ^{o}C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.46 (d, *J* = 4.8 Hz, 1H), 7.84 (s, 1H), 7.55 (td, *J* = 7.5, 1.3 Hz, 1H), 7.48 (d, *J* = 8.2 Hz, 1H), 7.46–7.39 (m, 2H), 7.13–7.05 (m, 2H), 5.98 (br s, 1H), 4.96 (dd, *J* = 7.8, 4.5 Hz, 1H), 2.97 (t, *J* = 6.6 Hz, 2H), 2.31–2.17 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 161.4, 148.6, 142.9, 136.9, 133.4, 132.8, 128.0, 127.7, 126.0, 125.5, 124.2, 123.3, 121.3, 73.7, 38.0, 34.5; **IR** (neat) 3250, 3054, 2919 cm^{-1}; **HRMS** (TOF MS ES+) *m* / *z* calcd for $C_{18}H_{17}ONNa$ $(M + Na)^+$ 286.1208, found 286.1199.

[8] Attar, S.; O'Brien, Z.; Alhaddad, H.; Golden, M. L.; Calderon-Urrea, A. *Bioorg. Med. Chem.* **2011**, *19*, 2055.
[9] Hattori, K.; Sajiki, H.; Hirota, K. *Tetrahedron* **2001**, *57*, 4817.

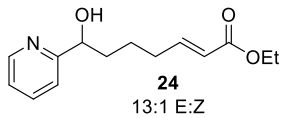
iii. Synthesis of Substrates 24 and 26 for Scheme 5

Compounds **24** and **26** were prepared by cross-metathesis of the corresponding alcohols with ethyl acrylate. In general, yields in the cross-metathesis step were higher and more reproducible when the alcohol was protected as the TBDMS ether (cf Scheme SI-1a and b).

Scheme SI-1 Synthesis of **24.**



SI-10. Using General Procedure A, outlined above, the following amounts of reagents were used: 2-pyridinecarboxaldehyde (0.95 mL, 10 mmol, 1.0 equiv), pent-4-en-1-ylmagnesium bromide (1.1 M in THF, 10 mL, 11 mmol, 1.1 equiv), and THF (15 mL). The product was purified by column flash chromatography (20–40% EtOAc/hexanes) to afford the title compound as a yellow oil (0.784 g, 4.40 mmol, 44%). **TLC R_f** = 0.4 (40% EtOAc/hexanes, UV active); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.53 (d, *J* = 4.5 Hz, 1H), 7.68 (td, *J* = 7.6, 1.5 Hz, 1H), 7.25 (d, *J* = 8.1 Hz, 1H), 7.19 (dd, *J* = 6.9, 5.1 Hz, 1H), 5.79 (ddt, *J* = 17.1, 10.3, 6.7 Hz, 1H), 4.99 (dd, *J* = 17.1, 1.6 Hz, 1H), 4.94 (d, *J* = 10.3 Hz, 1H), 4.80–4.78 (m, 1H), 4.25 (s, 1H), 2.16–2.02 (m, 2H), 1.89–1.78 (m, 1H), 1.74–1.62 (m, 1H), 1.58–1.47 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.3, 148.3, 138.8, 136.8, 122.4, 120.4, 114.7, 72.7, 38.1, 33.8, 24.6; **IR** (neat) 3260, 2936, 1594 cm^{-1}; **HRMS** (TOF MS ES+) *m* / *z* calcd for $C_{11}H_{15}ONNa$ $(M + Na)^+$ 200.1051, found 200.1056.

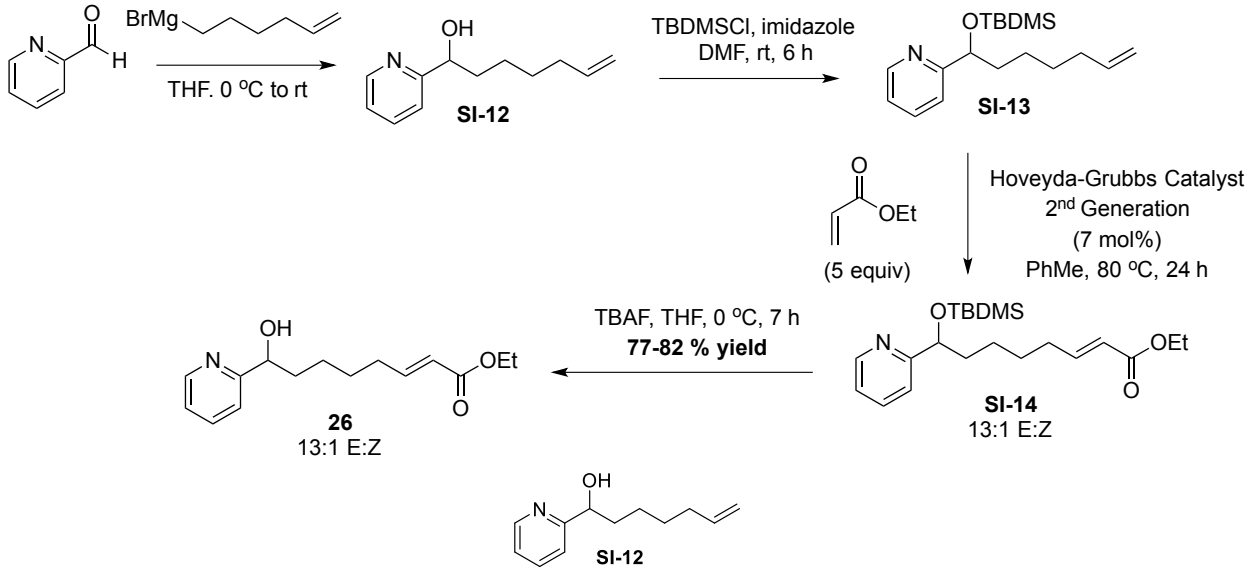


24. The title compound was prepared according to a modified procedure reported by Grubbs.[10] In a glovebox, a flame-dried bomb flask was charged with a stir bar, **SI-10** (0.71 g, 4.0 mmol, 1.0 equiv), and Hoveyda-Grubbs Catalyst 2nd Generation (178 mg, 0.280 mmol, 0.0700 equiv). The flask was removed from the glovebox, and anhydrous CH_2Cl_2 (50 mL) and ethyl acrylate (2.2 mL,

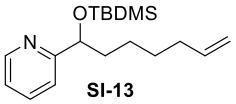
[10] Chatterjee, A. K.; Choi, T.–L.; Sanders, D. P.; Grubbs, R. H. *J. Am. Chem. Soc.* **2003**, *125*, 11360.

20 mmol, 5.0 equiv) were added. The flask was sealed and heated to reflux over 24 h. The flask was then cooled to ambient temperature, and the solvent was removed in vacuo. The residue was purified by flash column chromatography to afford the title compound as a pale yellow oil (125 mg, 0.501 mmol, 13%, 13:1 E:Z). **TLC R_f** = 0.1 (40% EtOAc/hexanes, UV active); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.53 (d, *J* = 4.4 Hz, 1H), 7.68 (td, *J* = 7.6, 1.5 Hz, 1H), 7.26 (d, *J* = 7.7 Hz, 1H), 7.20 (dd, *J* = 6.9, 5. Hz, 1H), 6.93 (dt, *J* = 15.5, 7.1 Hz, 1H), 5.80 (dt, *J* = 15.5, 1.5 Hz, 1H), 4.75 (dd, *J* = 7.2, 4.3 Hz, 1H), 4.33 (br s, 1H), 4.16 (q, *J* = 7.2 Hz, 2H), 2.28–2.18 (m, 2H), 1.90–1.81 (m, 1H), 1.75–1.66 (m, 1H), 1.64–1.55 (m, 2H), 1.28 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.8, 162.0, 148.9, 148.3, 136.8, 122.4, 121.7, 120.4, 72.5, 60.2, 38.0, 32.1, 23.7, 14.3; **IR** (neat) 2938, 1730 cm^{-1}; **HRMS** (TOF MS ES+) *m* / *z* calcd for $C_{14}H_{19}NO_3Na$ $(M + Na)^+$ 272.1263, found 272.1271.

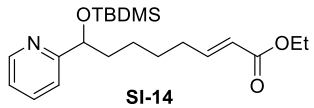
Scheme SI-2. Synthesis of **26.**



SI-12. Using General Procedure A, outlined above, the following amounts of reagents were used: 2-pyridinecarboxaldehyde (4.3 mL, 45 mmol, 1.0 equiv), hex-5-en-1-ylmagnesium bromide (1.1 M in THF, 50 mL, 50 mmol, 1.1 equiv), and THF (60 mL). The product was purified by column flash chromatography (20–40% EtOAc/hexanes) to afford the title compound as a yellow oil (4.4 g, 23.6 mmol, 53%).

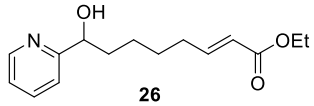


SI-13. Following the synthetic route outlined in Scheme SI-2, **SI-12** (2.0 g, 10 mmol, 1.0 equiv) was dissolved in DMF (20 mL) with TBDMSCl (12 mmol, 1.8 g, 1.2 equiv) and stirred at room temperature for 6 h. The crude reaction mixture was diluted with EtOAc (60 mL), washed with water (3x100 mL), then brine (3x100 mL) to remove DMF, dried over $MgSO_4$, and the solvent was removed to afford the product as a pale yellow oil (2.8 g, 9.3 mmol, 93%). The compound was taken forward without further purification.



SI-14
13:1 E:Z

SI-14. The title compound was prepared according to a modified procedure reported by Grubbs.[9] In a glovebox, a flame-dried bomb flask was charged with a stir bar, **SI-13** (1.5 g, 5.0 mmol, 1.0 equiv), and Hoveyda-Grubbs Catalyst 2nd Generation (350 mg, 0.560 mmol, 0.7 mol %). The flask was removed from the glovebox, and anhydrous PhMe (50 mL) and ethyl acrylate (2.7 mL, 25 mmol, 5.0 equiv) were added. The flask was sealed and heated to reflux over 24 h. The flask was then cooled to ambient temperature, and the solvent was removed in vacuo. The residue was purified by flash column chromatography (10-20% EtOAc/Hex) to afford the title compound as a pale yellow oil (1.45 g, 3.85 mmol, 77%, 13:1 *E:Z*).

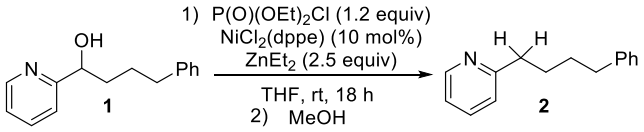


26
13:1 E:Z

26. SI-14 (1.0 g, 2.6 mmol, 1.0 equiv) was dissolved in THF (20 mL) and cooled to 0 °C. TBAF (1.0 M in THF, 3.6 mL, 3.6 mmol, 1.4 equiv) was then added slowly and the reaction was stirred for 5 to 7 h until judged complete by TLC. The reaction mixture was diluted with EtOAc (45 mL) and washed with saturated NH_4Cl (30 mL), water (30 mL), brine (30 mL), dried over $MgSO_4$, and the solvent was removed. The residue was purified by flash column chromatography (10-20% EtOAc, 3% triethyl amine in hexanes) to afford the title compound as a pale yellow oil. **TLC R_f** = 0.1 (1% TEA, 20% EtOAc/hexanes, UV active) **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.54 (m,1H), 7.7 (td, *J* = 7.7 Hz, 1.7 Hz, 1H), 7.22 (m, 2H), 6.9 (dt, *J* = 15.6, 7.0 Hz, 1H), 5.8 (dt, *J* = 15.6, 1.6 Hz, 1H), 4.7 (m, 1H), 4.2 (m, 1H), 2.2 (m, 1H), 1.8 (m, 1H), 1.7(m, 1H), 1.5(m, 1H), 1.3 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.7, 162.8, 149.2, 148.2, 136.8, 122.3, 121.4, 120.3, 72.9, 60.1, 38.2, 32.1, 28.0, 24.9, 14.3; **HRMS** (TOF MS ES+) *m* / *z* calcd for $C_{15}H_{21}NO_3Na$ $(M + Na)^+$ 286.1419, found 286.1414.

III. Nickel-Catalyzed Hydrogenolysis of Benzylic Carbinols and Characterization Data for Products

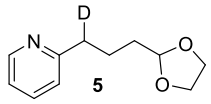
General Procedure B. *Hydrogenolysis of benzylic carbinols*



2. In a glovebox, a flame-dried 7 mL vial equipped with a stir bar was charged with $NiCl_2$(dppe) (11 mg, 0.020 mmol, 10 mol %), alcohol **1** (45 mg, 0.20 mmol, 1.0 equiv) and diethyl chlorophosphate (35 μL, 0.24 mmol, 1.2 equiv) and suspended in THF (1.6 mL). The reaction vial was capped with a screw-cap fitted with a septum and removed from the glove box. The reaction was placed under an atmosphere of N_2 and stirred at room temperature for five minutes. Diethyl zinc (1 M in PhMe, 0.50 mL, 0.50 mmol, 2.5 equiv) was added via syringe and an immediate color change from slightly orange to transparent yellow occurred. The reaction was then sealed with parafilm and allowed to stir for 18 h at 24 °C after which the reaction typically became dark brown or black. The reaction was quenched with MeOH and filtered through a plug of silica gel (washing with 100% EtOAc). The solvent was removed under reduced vacuum and the product was purified by flash column chromatography (12% EtOAc, 1% triethyl amine in hexanes) to afford the title compound as a pale yellow oil (29 mg, 0.13 mmol, 69%). **TLC R_f** = 0.3 (20% EtOAc/hexanes, UV active); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.52 (ddd, *J* = 4.9, 1.9, 1.0 Hz, 1H), 7.56 (td, *J* = 2.0, 7.7 Hz, 1H), 7.29–7.23 (m, 2H), 7.19–7.14 (m, 3H), 7.13–7.06 (m, 2H), 2.81 (t, *J* = 7.3 Hz, 2H), 2.65 (t, *J* = 7.7 Hz, 2H), 1.83–1.74 (m, 2H) 1.74–1.64 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.2, 149.3, 142.6, 136.3, 128.5, 128.3, 125.7, 122.7, 120.9, 38.3, 35.8, 31.3, 29.6; **IR** (neat) 3025, 2926, 2855, 2359, 2341, 1598 cm^{-1}; **HRMS** (TOF MS CI+) *m* / *z* calcd for $C_{16}H_{18}ONH_4$ $(M + NH_4)^+$ 211.1361, found 211.1351.

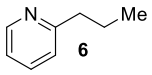
One-gram scale formation of 2. In a glovebox, a flame-dried round-bottomed flask equipped with a stir bar was charged with $NiCl_2$(dppe) (244.4 mg, 0.4444 mmol, 10 mol %), alcohol **1** (1.00 g, 4.44 mmol, 1.0 equiv) and diethyl chlorophosphate (777 μL, 5.33 mmol, 1.2 equiv) and suspended in THF (35.5 mL). The flask was capped with a septum and removed from the glove box. The reaction was placed under an atmosphere of N_2 and stirred at room temperature. Diethyl zinc (1 M in PhMe, 11.1 mL, 11.1 mmol, 2.5 equiv) was added via syringe and an immediate color change from slightly orange to transparent yellow occurred. The reaction was allowed to stir for 18 h at 24 °C after which the reaction typically became dark brown or black. The reaction was quenched with MeOH and filtered through a plug of silica gel (washing with 100% EtOAc). The solvent was removed under reduced vacuum and the product was purified by flash column chromatography (12% EtOAc, 1% triethyl amine in hexanes) to afford the title compound as a pale yellow oil (0.672 g, 3.01 mmol, 72%).

i. Deuterium incorporation (Scheme 2)

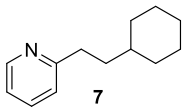


5. Using General Procedure B, outlined above, the following amounts of reagents were used: $NiCl_2$(dppe) (11 mg, 0.020 mmol, 10 mol %), alcohol **3** (42 mg, 0.20 mmol, 1.0 equiv), diethyl chlorophosphate (35 μL, 0.24 mmol, 1.2 equiv), THF (1.6 mL), and diethyl zinc (1.0 M in PhMe, 0.50 mL, 0.50 mmol, 2.5 equiv). The reaction was quenched with CH_3OD from a sealed ampoule (1 mL) and the product was purified by flash column chromatography (12 % EtOAc, 1% triethyl amine, in hexane) to afford the title compound as a pale yellow oil (30 mg, 0.15 mmol, 78%). **TLC R_f** = 0.1 (20% EtOAc/hexanes, UV active); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.52 (d, *J* = 4.6 Hz, 1H), 7.58 (td, *J* = 7.7, 1.9 Hz, 1H), 7.15 (d, *J* = 7.7 Hz, 1H), 7.11–7.08 (m, 1H), 4.89 (t, *J* = 4.7 Hz, 1H), 4.01–3.79 (m, 4H), 2.87–2.79 (m, 1H), 1.91–1.83 (m, 2H), 1.76–1.68 (m, 2H); **^{2}H NMR** (500 MHz, $CHCl_3$) 3.10 (s, 1D); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 161.8, 149.3, 136.3, 122.8, 121.1, 104.5, 64.9, 38.1, 33.4, 24.2; **IR** (neat) 2922, 2874, 1591, 1567, 1473, 1410 cm^{-1}; **HRMS** (TOF MS CI+) *m* / *z* calcd for $C_{16}H_{18}ONH_4$ $(M + NH_4)^+$ 195.1244, found 195.1251.

ii. Synthesis of Products in Scheme 3 (6–14)



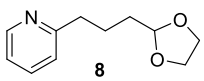
6. Using General Procedure B, outlined above, the following amounts of reagents were used: $NiCl_2$(dppe) (11 mg, 0.020 mmol, 10 mol %), alcohol **SI-1** (28 mg, 0.20 mmol, 1.0 equiv), diethyl chlorophosphate (35 μL, 0.24 mmol, 1.2 equiv), THF (1.6 mL), and diethyl zinc (1.0 M in PhMe, 0.50 mL, 0.50 mmol, 2.5 equiv). The product was purified by flash column chromatography (15% EtOAc/hexanes) to afford the title compound as a pale yellow oil (16 mg, 0.13 mmol, 67%). Analytical data is consistent with literature values.[11] **TLC R_f** = 0.3 (20% EtOAc/hexanes, UV active); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.53 (d, *J* = 4.4 Hz, 1H), 7.58 (t, *J* = 7.7 Hz, 1H), 7.14 (d, *J* = 7.7 Hz, 1H), 7.09 (t, *J* = 6.5 Hz, 1H), 2.77 (t, *J* = 7.8 Hz, 2H), 1.76 (sextet, *J* = 7.7 Hz, 2H), 0.97 (t, *J* = 7.7 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.4, 149.3, 136.3, 122.9, 121.0, 40.5, 23.2, 14.0.



7. Using General Procedure B, outlined above, the following amounts of reagents were used: $NiCl_2$(dppe) (11 mg, 0.020 mmol, 10 mol %), alcohol **SI-2** (41 mg, 0.20 mmol, 1.0 equiv), diethyl chlorophosphate (35 μL, 0.24 mmol, 1.2 equiv), THF (1.6 mL), and diethyl zinc (1.0 M in PhMe, 0.50 mL, 0.50 mmol, 2.5 equiv). The product was purified by flash column chromatography (15% EtOAc/hexanes) to afford the title compound as a pale yellow oil (27 mg, 0.14 mmol, 70%). **TLC R_f** = 0.2 (10% EtOAc/hexanes, UV active); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.52 (d, *J* = 4.5 Hz, 1H), 7.57 (td, *J* = 7.7, 1.7 Hz, 1H), 7.14 (d, *J* = 7.7 Hz, 1H), 7.08 (dd, *J* = 7.7, 5.2 Hz, 1H), 2.83–2.76 (m, 2H), 1.78 (ad, *J* = 13.3 Hz, 2H), 1.74–1.67 (m, 2H), 1.67–1.58 (m, 3H), 1.34–1.10 (m, 4H),

[11] Groenhagen, U.; Maczka, M.; Dickschat, J. S.; Schulz, S. *Beilstein J. Org. Chem.* **2014**, *10*, 1421.

1.00–0.90 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 163.0, 149.3, 136.4, 122.8, 120.9, 37.8, 37.7, 36.0, 33.4, 26.8, 26.5; **IR** (neat) 2920, 1589 cm^{-1}; **HRMS** (TOF MS ES+) *m* / *z* calcd for $C_{13}H_{19}NH$ $(M + H)^+$ 190.1596, found 190.1594.



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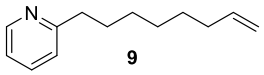
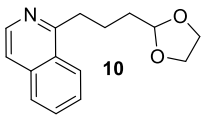
8. Using General Procedure B, outlined above, the following amounts of reagents were used: $NiCl_2$(dppe) (11 mg, 0.020 mmol, 10 mol %), alcohol **3** (42 mg, 0.20 mmol, 1.0 equiv), diethyl chlorophosphate (35 μL, 0.24 mmol, 1.2 equiv), THF (1.6 mL), and diethyl zinc (1.0 M in PhMe, 0.50 mL, 0.50 mmol, 2.5 equiv). The product was purified by flash column chromatography (12% EtOAc/hexanes) to afford the title compound as a pale yellow oil (31 mg, 0.15 mmol, 74 %). Analytical data are consistent with literature values.[12] **TLC R_f** = 0.1 (20% EtOAc/hexanes, UV active); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.52 (d, *J* = 4.9 Hz, 1H), 7.57 (td, *J* = 7.6, 1.6 Hz, 1H), 7.14 (d, *J* = 7.8 Hz, 1H), 7.10 (dd, *J* = 7.6, 5.3 Hz, 1H), 4.89 (t, *J* = 6 Hz, 1H), 4.00–3.79 (m, 4H), 2.84 (t, *J* = 7.7 Hz, 2H), 1.92–1.82 (m, 2H), 1.76–1.68 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 161.8, 149.3, 136.3, 122.8, 121.1, 104.5, 64.9, 38.1, 33.4, 24.2.



9

9. Using General Procedure B, outlined above, the following amounts of reagents were used: $NiCl_2$(dppe) (11 mg, 0.020 mmol, 10 mol %), alcohol **SI-3** (41 mg, 0.20 mmol, 1.0 equiv), diethyl chlorophosphate (35 μL, 0.24 mmol, 1.2 equiv), THF (1.6 mL), and diethyl zinc (1.0 M in PhMe, 0.50 mL, 0.50 mmol, 2.5 equiv). The product was purified by flash column chromatography (15% EtOAc/hexanes) to afford the title compound as a pale yellow oil (29 mg, 0.15 mmol, 77%). **TLC R_f** = 0.2 (20% EtOAc/hexanes, UV active); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.52 (d, *J* = 4.5 Hz, 1H), 7.58 (td, *J* = 7.6, 1.5 Hz, 1H), 7.14 (d, *J* = 7.6 Hz, 1H), 7.09 (dd, *J* = 7.3, 5.5 Hz, 1H), 5.80 (ddt, *J* = 17.1, 10.4, 3.3 Hz, 1H), 4.98 (dd, *J* = 17.1, 1.1 Hz, 1H), 4.92 (d, *J* = 10.4 Hz, 1H), 2.78 (t, *J* = 7.8 Hz, 2H), 2.03 (dd, *J* = 13.5, 6.5 Hz, 2H), 1.72 (quint, *J* = 7.6 Hz, 2H), 1.44–1.30 (m, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.2, 149.3, 139.3, 136.3, 122.8, 121.0, 114.3, 38.6, 33.9, 30.0, 29.6, 29.1, 28.9; **IR** (neat) 3075, 2925, 1589 cm^{-1}; **HRMS** (TOF MS ES+) *m* / *z* calcd for $C_{13}H_{19}NNa$ $(M + Na)^+$ 212.1415, found 212.1406.

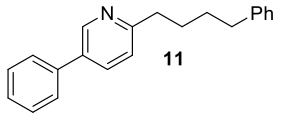


10

10. Using General Procedure B, outlined above, the following amounts of reagents were used: $NiCl_2$(dppe) (11 mg, 0.020 mmol, 10 mol %), alcohol **SI-4** (52 mg, 0.20 mmol, 1.0 equiv), diethyl chlorophosphate (35 μL, 0.24 mmol, 1.2 equiv), THF (1.6 mL), and diethyl zinc (1.0 M in PhMe, 0.50 mL, 0.50 mmol, 2.5 equiv). The product was purified by flash column chromatography (30–50% EtOAc/hexanes) to afford the title compound as a pale yellow oil (24 mg, 0.099 mmol, 49%). **TLC R_f** = 0.2 (40% EtOAc/hexanes, UV active); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.43 (d, *J* = 5.6

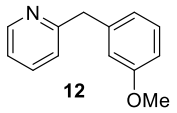
[12] Kitbunnadaj, R.; Zuiderveld, O.P.; Christophe, B.; Hulscher, S.; Menge, W.M.P.B.; Gelens, E.; Snip, E.; Bakker, R.A.; Celanire, S.; Gillard, M.; Talaga, P.; Timmerman, H.; Leurs, R. *J. Med. Chem*. **2004**, *47*, 2414.

Hz, 1H), 8.17 (d, *J* = 8.4 Hz, 1H), 7.81 (d, *J* = 8.4 Hz, 1H), 7.66 (t, *J* = 7.5 Hz, 1H), 7.59 (t, *J* = 7.5 Hz, 1H), 7.50 (d, *J* = 5.6 Hz, 1H), 4.93 (t, *J* = 4.7 Hz, 1H), 4.00–3.92 (m, 2H), 3.89–3.81 (m, 2H), 3.36 (t, *J* = 8.0 Hz, 2H), 2.07–1.98 (m, 2H) 1.88–1.81 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 161.9, 142.1, 136.4, 129.9, 127.5, 127.14, 127.05, 125.4, 119.4, 104.5, 65.0, 35.2, 33.8, 24.1; **IR** (neat) 3050, 2877, 1562 cm^{-1}; **HRMS** (TOF MS ES+) *m* / *z* calcd for $C_{15}H_{17}O_2NNa$ $(M + Na)^+$ 266.1157, found 266.1160.



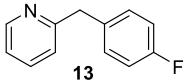
11

11. Using General Procedure B, outlined above, the following amounts of reagents were used: $NiCl_2$(dppe) (11 mg, 0.020 mmol, 10 mol %), alcohol **SI-6** (61 mg, 0.20 mmol, 1.0 equiv), diethyl chlorophosphate (35 μL, 0.24 mmol, 1.2 equiv), THF (1.6 ML), and diethyl zinc (1.0 M in PhMe, 0.50 mL, 0.50 mmol, 2.5 equiv). The product was purified by flash column chromatography (30–50% EtOAc/hexanes) to afford the title compound as a white solid (48 mg, 0.17 mmol, 83%). **TLC R_f** = 0.2 (10% EtOAc/hexanes, UV active); **m.p.** = 60 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.75 (s, 1H), 7.76 (dd, *J* = 8.1, 2.0 Hz, 1H), 7.56 (d, *J* = 8.0 Hz, 2H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.37 (t, *J* = 7.2 Hz, 1H), 7.26 (t, *J* = 7.5 Hz, 2H), 7.18 (d, *J* = 8.1 Hz, 4H), 2.86 (t, *J* = 8.2 Hz, 2H), 2.67 (t, *J* = 7.6 Hz, 2H), 1.82 (quint, *J* = 7.6 Hz, 2H), 1.72 (quint, *J* = 7.5 Hz, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 161.1, 147.7, 142.6, 138.0, 134.8, 134.0, 129.1, 128.5, 128.4, 127.9, 127.1, 125.8, 122.7, 38.0, 35.9, 31.3, 29.6; **IR** (neat) 3056, 2854 cm^{-1}; **HRMS** (TOF MS ES+) *m* / *z* calcd for $C_{21}H_{21}NH$ $(M + H)^+$ 288.1752, found 288.1758.



12

12. Using General Procedure B, outlined above, the following amounts of reagents were used: $NiCl_2$(dppe) (11 mg, 0.020 mmol, 10 mol %), alcohol **SI-7** (43 mg, 0.20 mmol, 1.0 equiv), diethyl chlorophosphate (35 μL, 0.24 mmol, 1.2 equiv), THF (1.6 mL), and diethyl zinc (1.0 M in PhMe, 0.50 mL, 0.50 mmol, 2.5 equiv). The product was purified by flash column chromatography (20 % EtOAc, 10% DCM, in hexanes) to afford the title compound as a pale yellow oil (21.5 mg, 0.120 mmol, 54%). Analytical data are consistent with literature values.[13] **TLC R_f** = 0.3 (20% EtOAc/hexanes, UV active); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.54 (d, *J* = 4.3 Hz, 1H), 7.57 (td, *J* = 7.6, 1.7, 1H), 7.21 (t, *J* = 7.9 Hz, 1H), 7.12 (s, 1H), 7.10 (t, *J* = 3.2 Hz, 1H), 6.85 (d, *J* = 7.4 Hz, 1H), 6.81 (s, 1H), 6.76 (dd, *J* = 8.4, 2.4 Hz, 1H), 4.13 (s, 2H), 3.77 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 160.9, 159.8, 149.4, 141.1, 136.6, 129.6, 123.2, 121.5, 121.3, 114.9, 111.9, 55.2, 44.8.

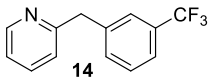


13

13. Using General Procedure B, outlined above, the following amounts of reagents were used: $NiCl_2$(dppe) (11 mg, 0.020 mmol, 10 mol %), alcohol **SI-8** (43 mg, 0.20 mmol, 1.0 equiv), diethyl chlorophosphate (35 μL, 0.24 mmol, 1.2 equiv), THF (1.6 mL), and diethyl zinc (1.0 M in PhMe, 0.50 mL, 0.50 mmol, 2.5 equiv). The crude product was pre-absorbed to a minimal amount of

[13] Chen, X.; Zhou, L.; Li, Y.; Xie, T.; Zhou, S. *J. Org. Chem.* **2014**, *79*, 230.

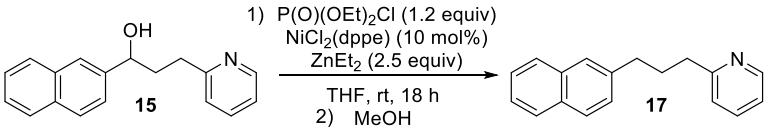
silica and purified by flash column chromatography (12 % EtOAc, 1% triethyl amine, in hexane) to afford the title compound as a pale yellow oil (20.3 mg, 0.120 mmol, 60%). Analytical data are consistent with literature values.[14] **TLC R_f** = 0.3 (20% EtOAc/hexanes, UV active); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.55 (ddd, *J* = 4.9, 1.9, 1.0 Hz, 1H), 7.58 (td, *J* = 7.6, 1.9 Hz, 1H), 7.24–7.19 (m, 2H), 7.14–7.07 (m, 2H), 7.01–6.95 (m, 2H), 4.12 (s, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.5 (d, J_{CF} = 244.14 Hz), 160.6, 149.4, 136.6, 135.1 (d, J_{CF} = 3.24 Hz), 130.5 (d, J_{CF} = 7.87 Hz), 123.0, 121.3, 115.3 (d, J_{CF} = 21.2 Hz), 43.8.



14

14. Using General Procedure B, outlined above, the following amounts of reagents were used: $NiCl_2$(dppe) (11 mg, 0.020 mmol, 10 mol %), alcohol **SI-9** (51 mg, 0.20 mmol, 1.0 equiv), diethyl chlorophosphate (35 μL, 0.24 mmol, 1.2 equiv), THF (1.6 mL), and diethyl zinc (1.0 M in PhMe, 0.50 mL, 0.50 mmol, 2.5 equiv). The product was purified by flash column chromatography (30–50% EtOAc/hexanes) to afford the title compound as a pale yellow oil (29.4 mg, 0.124 mmol, 62%). Analytical data are consistent with literature values.[10] **TLC R_f** = 0.2 (10% EtOAc/hexanes, UV active); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.56 (d, *J* = 4.9 Hz, 1H), 7.61 (dt, *J* = 2.0, 7.6 Hz, 1H), 7.53 (s, 1H), 7.50–7.38 (m, 3H), 7.17–7.09 (m, 2H), 4.21 (s, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 159.9, 149.6, 140.4, 136.8, 132.5, 130.8 (q, J_{CF} = 31.2 Hz), 129.0, 125.7, 124.2 (q, J_{CF} = 270 Hz) 123.4, 123.3, 121.6, 44.3.

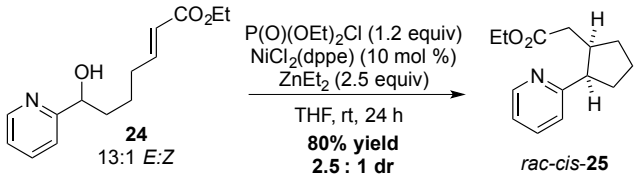
iii. Hydrogenolysis of 15 (Scheme 4)



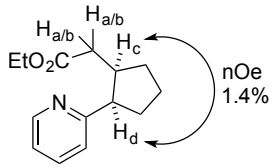
17. Using General Procedure B, outlined above, the following amounts of reagents were used: $NiCl_2$(dppe) (11 mg, 0.020 mmol, 10 mol %), alcohol **15** (55 mg, 0.20 mmol, 1.0 equiv), diethyl chlorophosphate (35 μL, 0.24 mmol, 1.2 equiv), THF (1.6 mL), and diethyl zinc (1.0 M in PhMe, 0.50 mL, 0.50 mmol, 2.5 equiv). The product was purified by flash column chromatography (20% EtOAc/hexanes) to afford the title compound as a pale yellow oil (40 mg, 0.16 mmol, 81%). **TLC R_f** = 0.2 (20% EtOAc/hexanes, UV active); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.54 (d, *J* = 4.4 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.76 (d, *J* = 7.7 Hz, 2H), 7.62 (s, 1H), 7.56 (t, *J* = 7.7 Hz, 1H), 7.47–7.38 (m, 2H), 7.34 (d, *J* = 8.3 Hz, 1H), 7.12 (d, *J* = 7.7 Hz, 1H), 7.09 (at, *J* = 6.4 Hz, 1H), 2.90–2.81 (m, 4H), 2.16 (quint, *J* = 7.0 Hz, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.0, 149.4, 139.8, 136.3, 133.7, 132.1, 128.0, 127.7, 127.53, 127.48, 126.6, 126.0, 125.2, 122.9, 121.1, 38.0, 35.8, 31.4; **IR** (neat) 3051, 2856, 1590 cm^{-1}; **HRMS** (TOF MS ES+) *m* / *z* calcd for $C_{18}H_{17}NNa$ $(M + Na)^+$ 270.1259, found 270.1260.

[14] De Houwer, J.; Tehrani, K. A.; Maes, B. U. W. *Angew. Chem. Int. Ed.* **2012**, *51*, 2745.

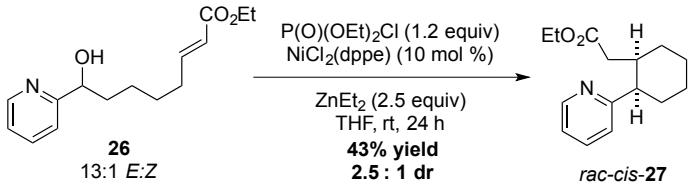
IV. Nickel-Catalyzed Intramolecular 1,4-addition (Scheme 5)



25. Using General Procedure B, outlined above, the following amounts of reagents were used: $NiCl_2$(dppe) (11 mg, 0.020 mmol, 10 mol %), alcohol **24** (50 mg, 0.20 mmol, 1.0 equiv), diethyl chlorophosphate (35 μL, 0.24 mmol, 1.2 equiv), THF (1.6 mL), and diethyl zinc (1.0 M in PhMe, 0.50 mL, 0.50 mmol, 2.5 equiv). The product was purified by flash column chromatography (20% EtOAc/hexanes) to afford the title compound as a 2.5:1 mixture of diastereomers (37 mg, 0.16 mmol, 80%). H_c was integrated to determine the ratio of diastereomers. Flash column chromatography (5–10% EtOAc/hexanes) was performed a second time to isolate analytically pure cis diastereomer (19 mg, 0.081 mmol, 40%) and a 1:1 mixture of diastereomers (16 mg, 0.070 mmol, 34%). The relative configuration of the cis diastereomer was assigned based on the nOe correlation shown.

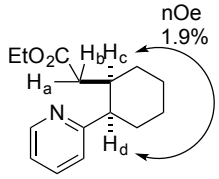


TLC R_f = 0.1 (10% EtOAc/hexanes, UV active); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.55 (d, *J* = 4.7 Hz, 1H), 7.56 (td, *J* = 7.7, 2.0 Hz, 1H), 7.12–7.07 (m, 2H), 4.00 (q, *J* = 7.2 Hz, 2H), 3.43 (q, *J* = 8.0 Hz, 1H), 2.79–2.71 (m, 1H), 2.14–2.04 (m, 2H), 2.02–1.90 (m, 4H), 1.75–1.67 (m, 1H), 1.63–1.54 (m, 1H), 1.17 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 173.6, 163.2, 149.2, 136.0, 123.5, 121.2, 60.2, 49.8, 40.8, 36.2, 31.9, 30.2, 24.2, 14.3; **IR** (neat) 2935, 1716 cm^{-1}; **HRMS** (TOF MS ES+) *m* / *z* calcd for $C_{14}H_{19}NO_2Na$ $(M + Na)^+$ 256.1313, found 256.1316.



27. Using General Procedure B, outlined above, the following amounts of reagents were used: $NiCl_2$(dppe) (11 mg, 0.020 mmol, 10 mol %), alcohol **26** (53 mg, 0.20 mmol, 1.0 equiv), diethyl chlorophosphate (35 μL, 0.24 mmol, 1.2 equiv), THF (1.6 mL), and diethyl zinc (1.0 M in PhMe, 0.50 mL, 0.50 mmol, 2.5 equiv). The product was purified by flash column chromatography (10-20% EtOAc/hexanes) to afford the title compound as a 2.5:1 mixture of diastereomers (21.3 mg, 0.086 mmol, 43%). H_c was integrated to determine the ratio of diastereomers. Flash column chromatography (5–10% EtOAc/hexanes) was performed a second time to isolate the

analytically pure cis diastereomer (11 mg, 0.045 mmol, 23%) and a 1:1 mixture of diastereomers (10 mg, 0.04 mmol, 20%). The relative configuration of the cis diastereomer was assigned based on the nOe correlation shown below.



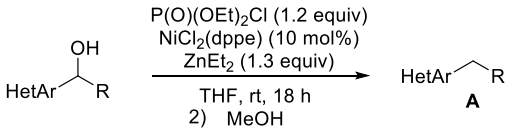
rac-cis-**27**

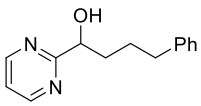
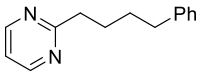
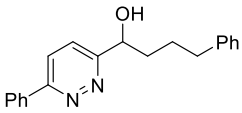
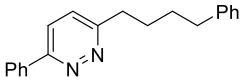
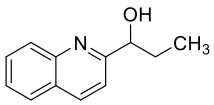
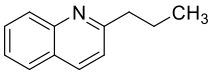
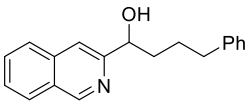
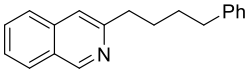
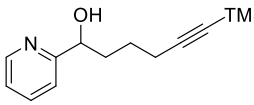
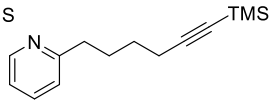
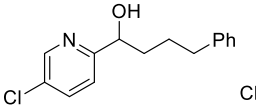
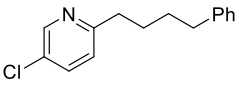
TLC R_f = 0.5 (20% EtOAc/hexanes, UV active); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.54 (d, *J* = 4.3 Hz, 1H), 7.59 (t, *J* = 7.6, Hz, 1H), 7.12–7.05 (m, 2H), 3.97 (q, *J* = 7.3 Hz, 2H), 3.05 (m, 1H), 2.7 (m, 1H), 2.34 (dd, *J* = 9.8, 5.38, 1H), 2.00 (dd, *J* = 4.3, 4.7 1H), 1.95–1.75 (m, 4H), 1.69 (m, 1H), 1.5 (m, 2H), 1.4 (m, 1H) 1.16 (t, *J* = 7.14 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 173.8, 164.3, 149.3, 136.4, 122.4, 121.4, 60.4, 48.1, 36.3, 32.8, 30.6, 26.2, 25.4, 21.0, 14.5; **HRMS** (TOF MS ES+) *m* / *z* calcd for $C_{15}H_{21}NO_2Na$ $(M + Na)^+$ 270.1470, found 270.1471.

IV. Additional Information Regarding Substrate Scope

The identity of the functional groups and heteroarenes of the benzylic alcohols were varied to explore the functional group tolerance of the reaction (Table SI-1). Heterocycles containing more than a single nitrogen, such as pyrimidine and pyridazine, formed the desired product in low yields (entries 1 and 2). Likewise, 2-quinoline and 3-isoquinoline moieties were not well tolerated under the reaction conditions (entries 3 and 4). A 2-pyridyl carbinol containing a tethered TMS protected alkyne produced the desired deoxygenated product in modest yield (entry 5). Finally, halogen substitution within the pyridine ring proved detrimental to the desired transformation (entry 6).

Table SI-1. Evaluation of additional substrate classes

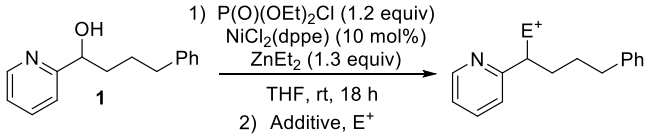


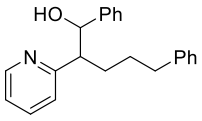
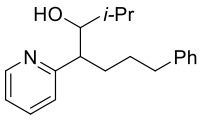
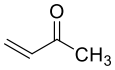
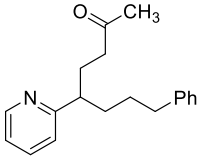
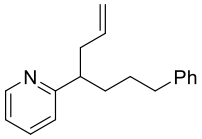
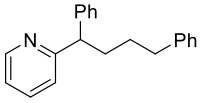
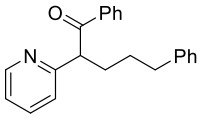
Entry	Substrate	Deoxygenation Product	yield **A** (%)[a]
1			8
1			16
3			11
4			20
5[b]			45
6			15

[a]Determined by ^{1}H NMR using an internal standard ($PhSiMe_3$).
[b]Reaction run at 70 °C

The addition of benzylic zinc reagents formed under our reaction conditions to a variety of electrophiles was examined (Table SI-2). Representative examples are shown. Titanium- and copper-assisted additions of zinc reagent into aldehydes proceeds in modest yield (entries 1 and 2). An intermolecular 1,4-addition to methyl vinyl ketone afford the desired product in 30% yield (entry 3). Addition of zinc reagent to allyl bromide resulted in low yield of the alkylated product (entry 4). Cross-coupling of the benzylic zinc reagent with iodobenzene failed to produce desired product (entry 5). Finally, nickel-catalyzed coupling of the zinc reagent with benzoyl chloride results in low yields of the desired ketone (entry 6).

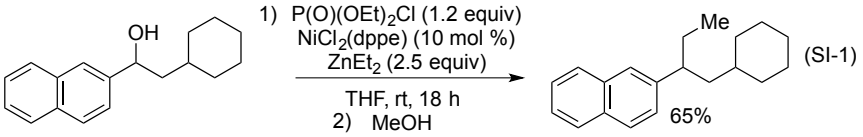
Table SI-2. Addition of heterobenzylic zinc reagent to electrophiles



Entry	Additive	E^+	Product	yield **A** (%)[a]
1	$Ti(O\textit{i}\text{-}Pr)_4$	PhCHO		21
2	CuCN•2LiCl	*i*-PrCHO		32
3	none			30
4	CuCN•2LiCl			12
5	none	PhI		< 5
6	none	benzoyl chloride		11

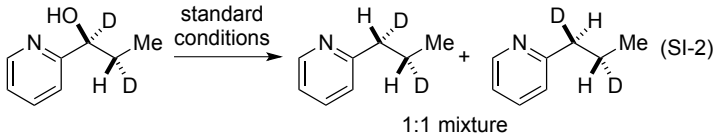
[a]Determined by ^{1}H NMR using an internal standard ($PhSiMe_3$).

In the absence of a pyridine directing group, simple Negishi cross-coupling occurs (eq SI-1).



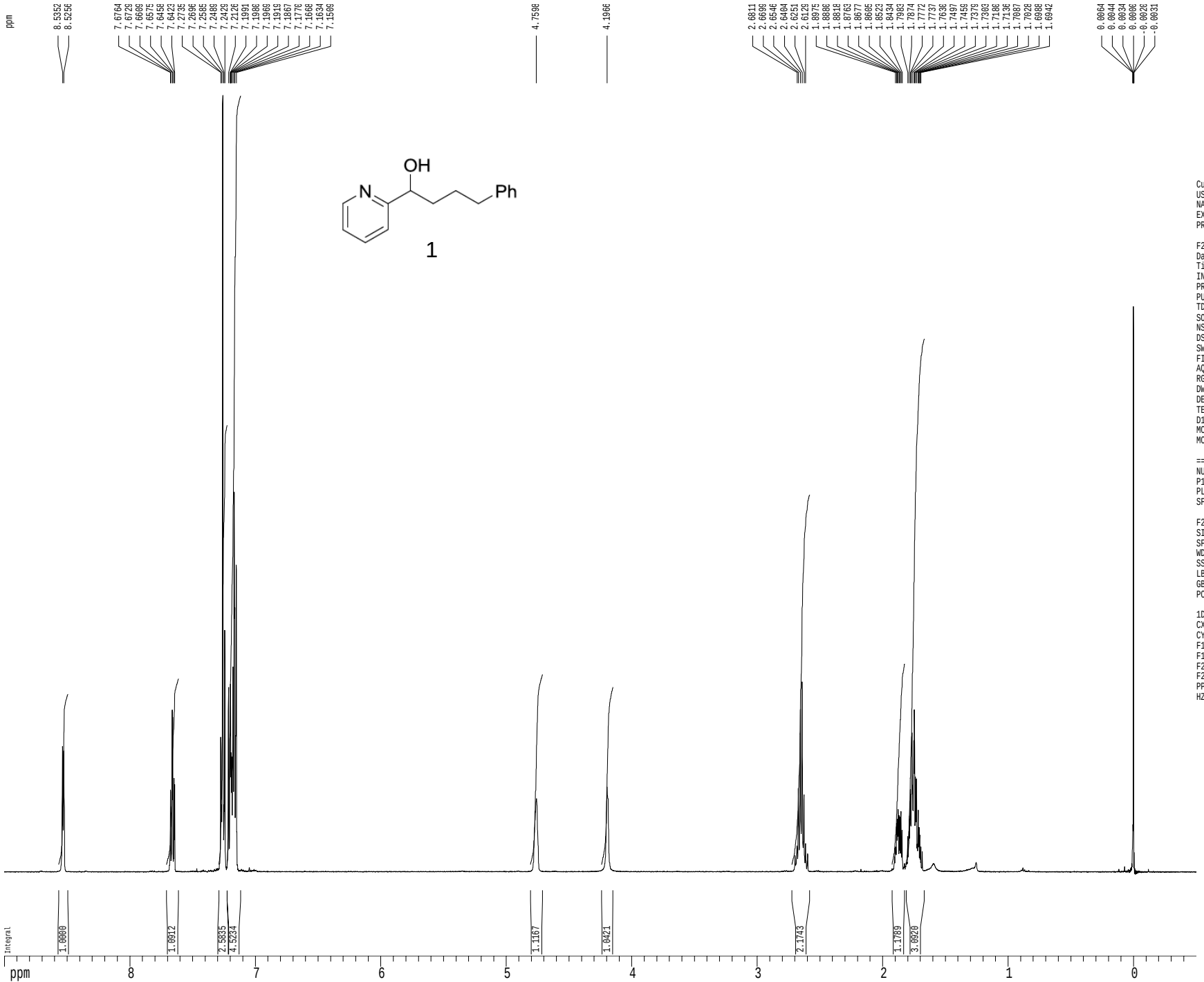
(SI-1)

The hydrogenolysis is stereoablative, as demonstrated by reduction of a deuterated test substrate.



(SI-2)

1H spectrum

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NAME      LEH-5-MRH-102-H1
EXPNO                1
PROCNO               1

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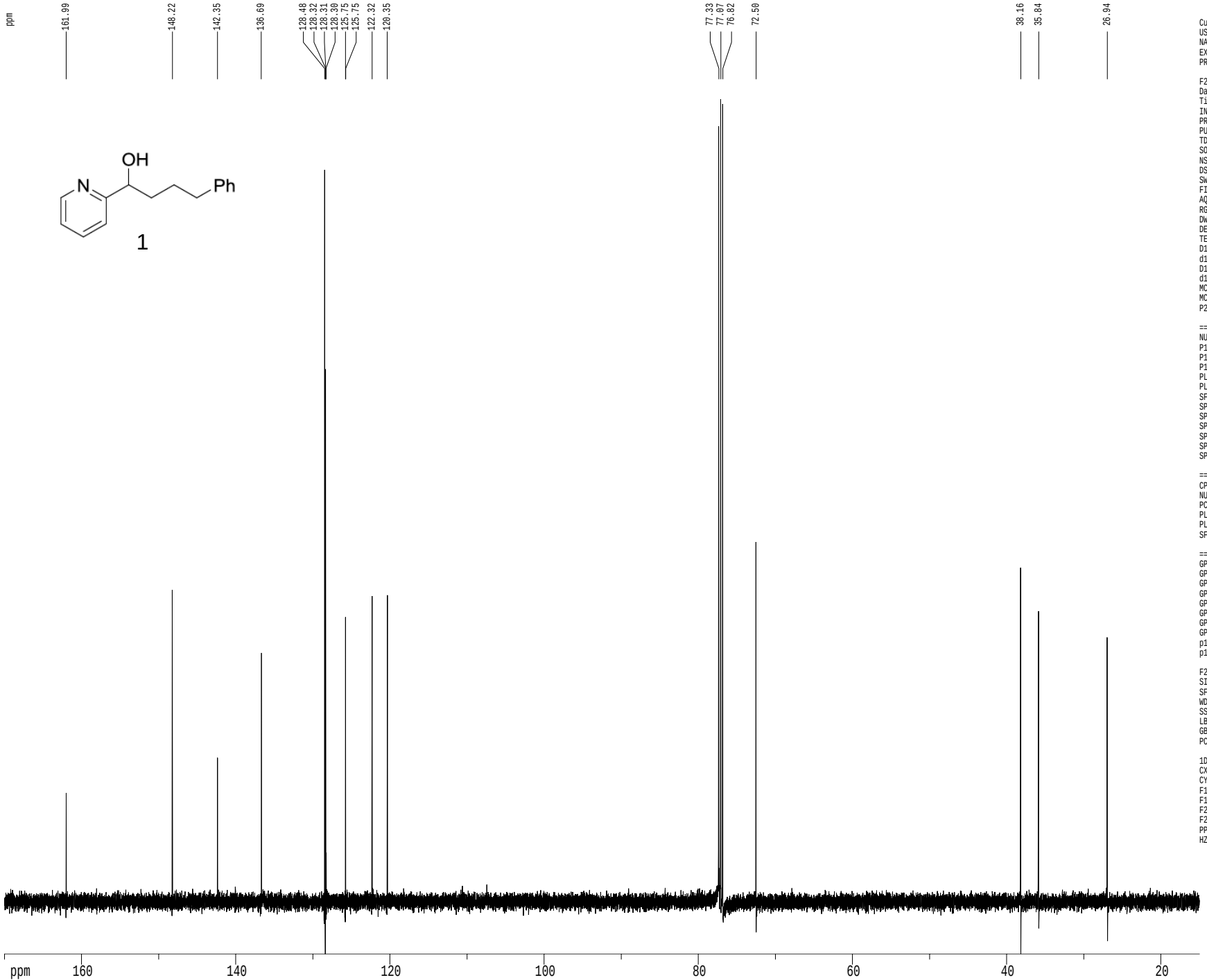
Time              18.59
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG            zg30
TD                32048
SOLVENT            CDCl3
NS                    8
DS                    2
SWH             8012.820 Hz
FIDRES          0.250026 Hz
AQ              1.9998451 sec
RG                  5.7
DW                62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                65536
SF          500.2200321 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 4.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P               9.000 ppm
F1              4501.98 Hz
F2P              -0.500 ppm
F2              -250.11 Hz
PPMCM          0.41667 ppm/cm
HZCM          208.42502 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



Current Data Parameters
USER lhanna
NAME LEH-5-MRH-102-C13
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20150114
Time 19.07
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG SpinEchopg30gp.prd
TD 65536
SOLVENT CDCl3
NS 513
DS 16
SWH 30303.031 Hz
FIDRES 0.462388 Hz
AQ 1.0813940 sec
RG 10321.3
DW 16.500 usec
DE 6.00 usec
TE 298.0 K
D1 0.25000000 sec
d11 0.03000000 sec
D16 0.00020000 sec
d17 0.00019600 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
P2 33.10 usec

======== CHANNEL f1 ========
NUC1 13C
P1 16.55 usec
P11 500.00 usec
P12 2000.00 usec
PL0 120.00 dB
PL1 -1.00 dB
SFO1 125.7942548 MHz
SP1 2.70 dB
SP2 2.70 dB
SPNAM1 Crp60,0.5,20.1
SPNAM2 Crp60comp.4
SPOFF1 0.00 Hz
SPOFF2 0.00 Hz

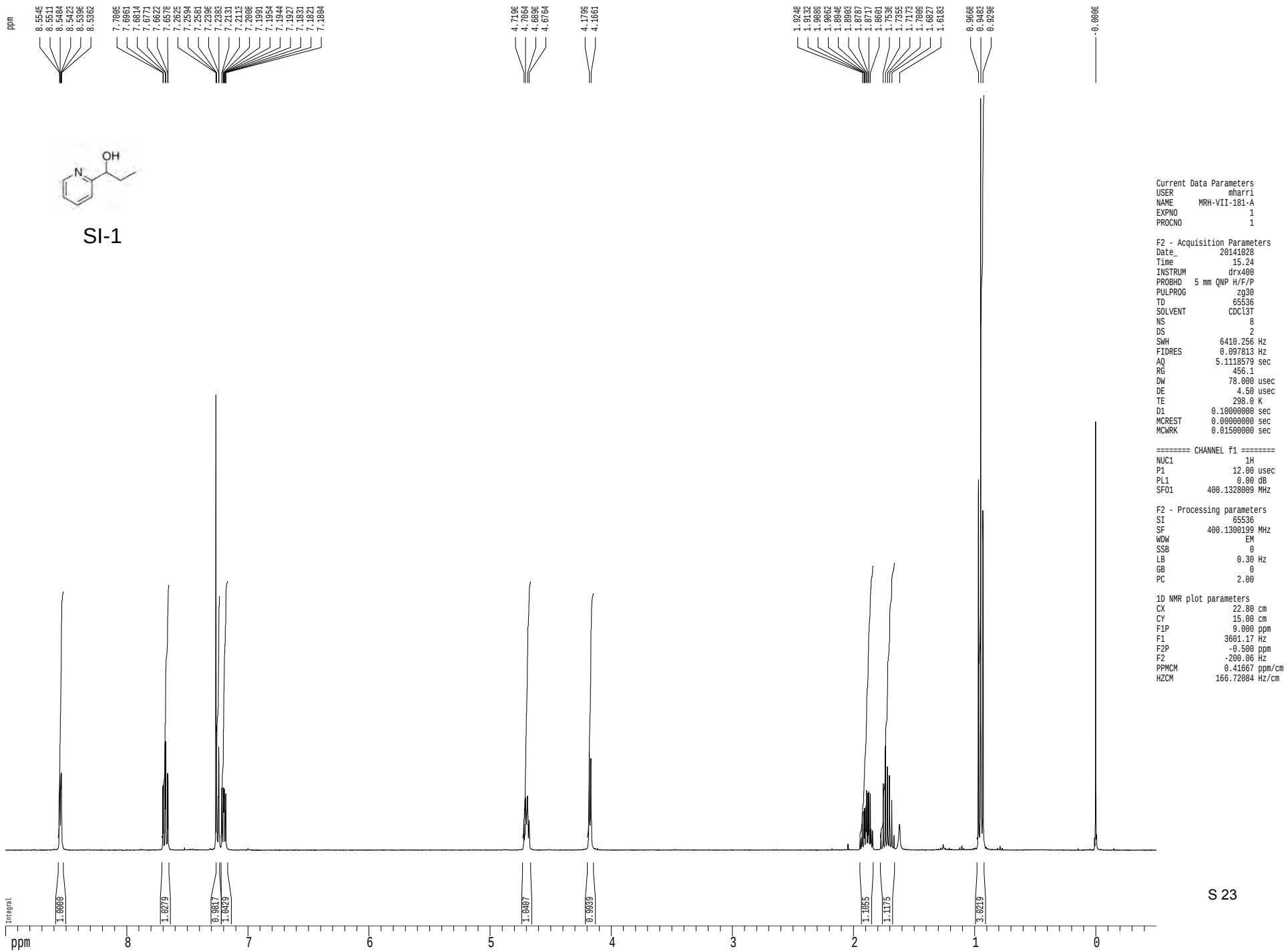
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 1.60 dB
PL12 24.50 dB
SFO2 500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1 SINE.100
GPNAM2 SINE.100
GPX1 0.00 %
GPX2 0.00 %
GPY1 0.00 %
GPY2 0.00 %
GPZ1 30.00 %
GPZ2 50.00 %
p15 500.00 usec
p16 1000.00 usec

F2 - Processing parameters
SI 65536
SF 125.7804190 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.80 cm
CY 15.65 cm
F1P 170.000 ppm
F1 21382.67 Hz
F2P 15.000 ppm
F2 1886.71 Hz
PPMCM 6.79825 ppm/cm
HZCM 855.08618 Hz/cm

1H spectrum

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NAME       MRH-VII-181-A
EXPNO                1
PROCNO               1

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Time              15.24
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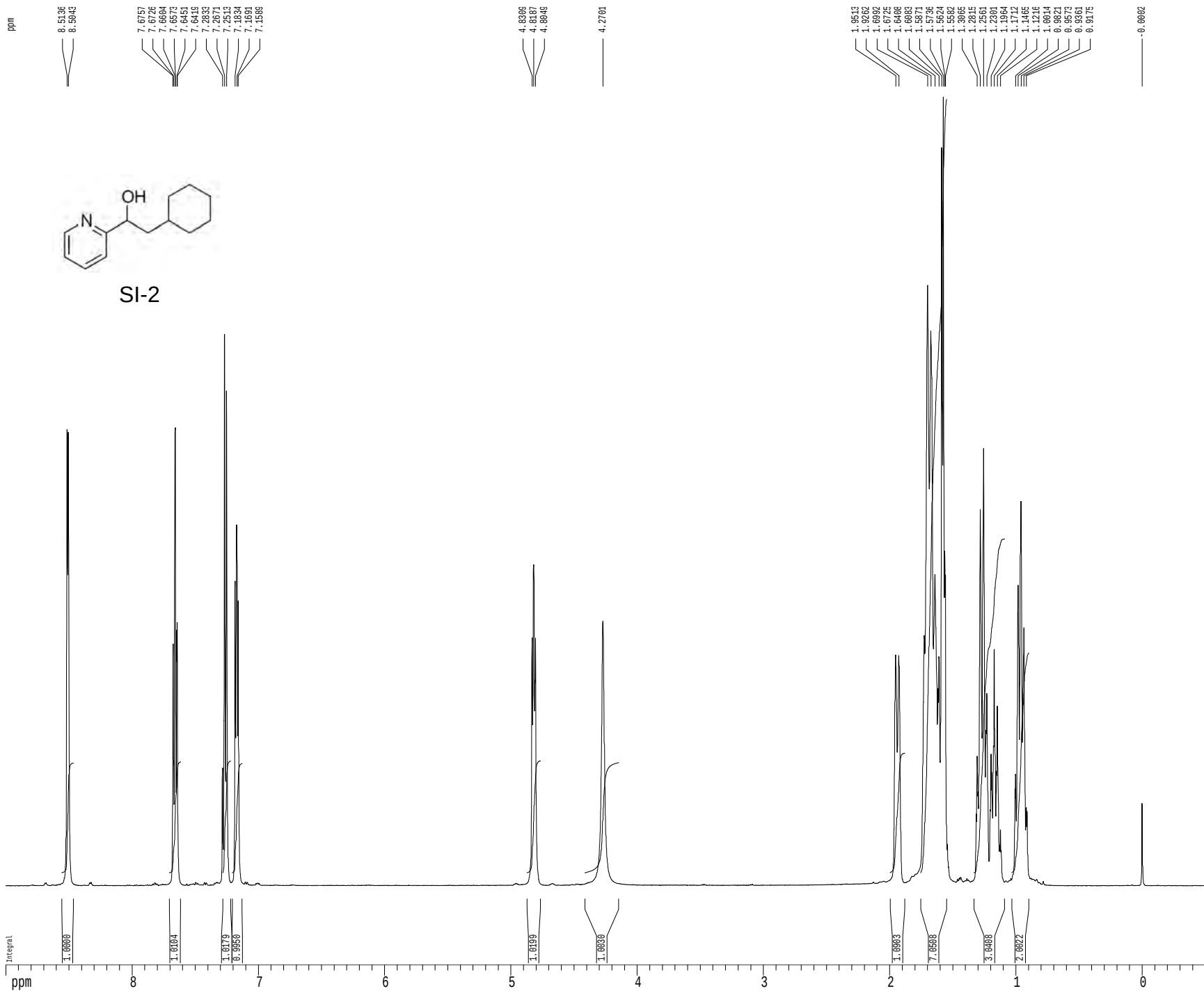
PROBHD   5 mm QNP H/F/P
PULPROG            zg30
TD                65536
SOLVENT           CDCl3T
NS                    8
DS                    2
SWH            6410.256 Hz
FIDRES        0.097813 Hz
AQ            5.1118579 sec
RG                456.1
DW               78.000 usec
DE                4.50 usec
TE                298.0 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                12.00 usec
PL1                0.00 dB
SFO1        400.1328009 MHz

F2 - Processing parameters
SI                65536
SF          400.1300199 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 2.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P               9.000 ppm
F1              3601.17 Hz
F2P              -0.500 ppm
F2              -200.06 Hz
PPMCM          0.41667 ppm/cm
HZCM          166.72084 Hz/cm
```

1H spectrum

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NAME      MRH-VII-299-1HNMR
EXPNO                    1
PROCNO                   1

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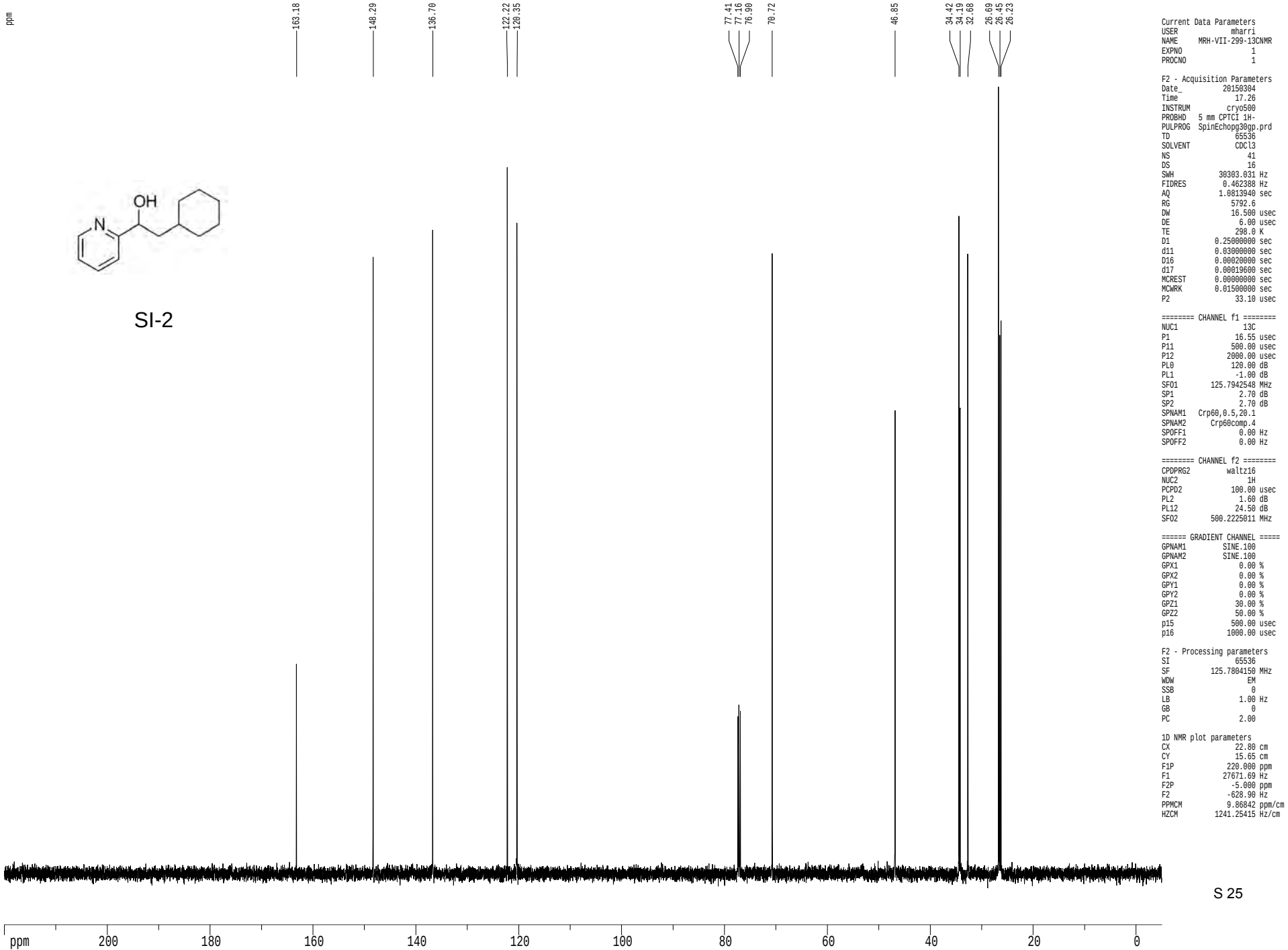
PROBHD   5 mm CPTCI 1H-
PULPROG               zg30
TD                   81728
SOLVENT              CDCl3
NS                       8
DS                       2
SWH               8012.820 Hz
FIDRES               0.098043 Hz
AQ                5.0998774 sec
RG                       5
DW                  62.400 usec
DE                   6.00 usec
TE                  298.0 K
D1              0.10000000 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec

======== CHANNEL f1 ========
NUC1                     1H
P1                    7.50 usec
PL1                   1.60 dB
SFO1          500.2235015 MHz

F2 - Processing parameters
SI                   65536
SF             500.2200197 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    4.00

1D NMR plot parameters
CX                   22.80 cm
CY                   15.00 cm
F1P                   9.000 ppm
F1                 4501.98 Hz
F2P                  -0.500 ppm
F2                 -250.11 Hz
PPMCM              0.41667 ppm/cm
HZCM             208.42502 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling

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Current Data Parameters
USER                mharri
NAME      MRH-VII-299-13CNMR
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_            20150304
Time                17.26
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                  65536
SOLVENT             CDCl3
NS                     41
DS                     16
SWH             30303.031 Hz
FIDRES          0.462388 Hz
AQ              1.0813940 sec
RG                 5792.6
DW                 16.500 usec
DE                  6.00 usec
TE                298.0 K
D1              0.25000000 sec
d11             0.03000000 sec
D16             0.00020000 sec
d17             0.00019600 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec
P2                  33.10 usec

======== CHANNEL f1 ========
NUC1                   13C
P1                  16.55 usec
P11                500.00 usec
P12               2000.00 usec
PL0                120.00 dB
PL1                 -1.00 dB
SFO1          125.7942548 MHz
SP1                 2.70 dB
SP2                 2.70 dB
SPNAM1   Crp60,0.5,20.1
SPNAM2      Crp60comp.4
SPOFF1                0.00 Hz
SPOFF2                0.00 Hz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2              100.00 usec
PL2                  1.60 dB
PL12                24.50 dB
SFO2          500.2225011 MHz

====== GRADIENT CHANNEL =====
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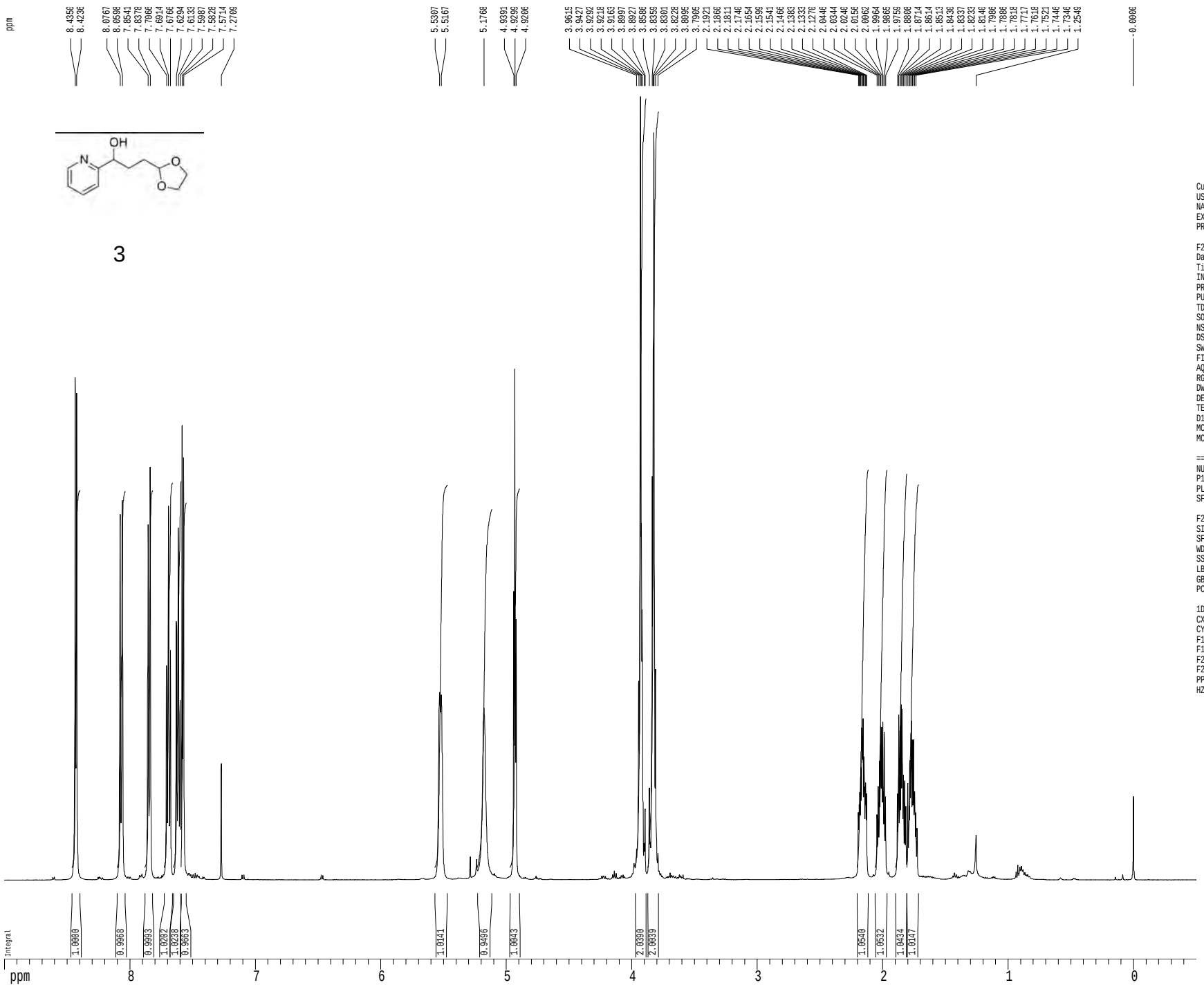
GPNAM2           SINE.100
GPX1                  0.00 %
GPX2                  0.00 %
GPY1                  0.00 %
GPY2                  0.00 %
GPZ1                 30.00 %
GPZ2                 50.00 %
p15                 500.00 usec
p16                1000.00 usec

F2 - Processing parameters
SI                    65536
SF            125.7804150 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    2.00

1D NMR plot parameters
CX                   22.80 cm
CY                   15.65 cm
F1P                220.000 ppm
F1               27671.69 Hz
F2P                 -5.000 ppm
F2                -628.90 Hz
PPMCM             9.86842 ppm/cm
HZCM           1241.25415 Hz/cm
```

1H spectrum

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Current Data Parameters
USER                mharri
NAME      MRH-VII-208-1HNMR
EXPNO                    1
PROCNO                   1

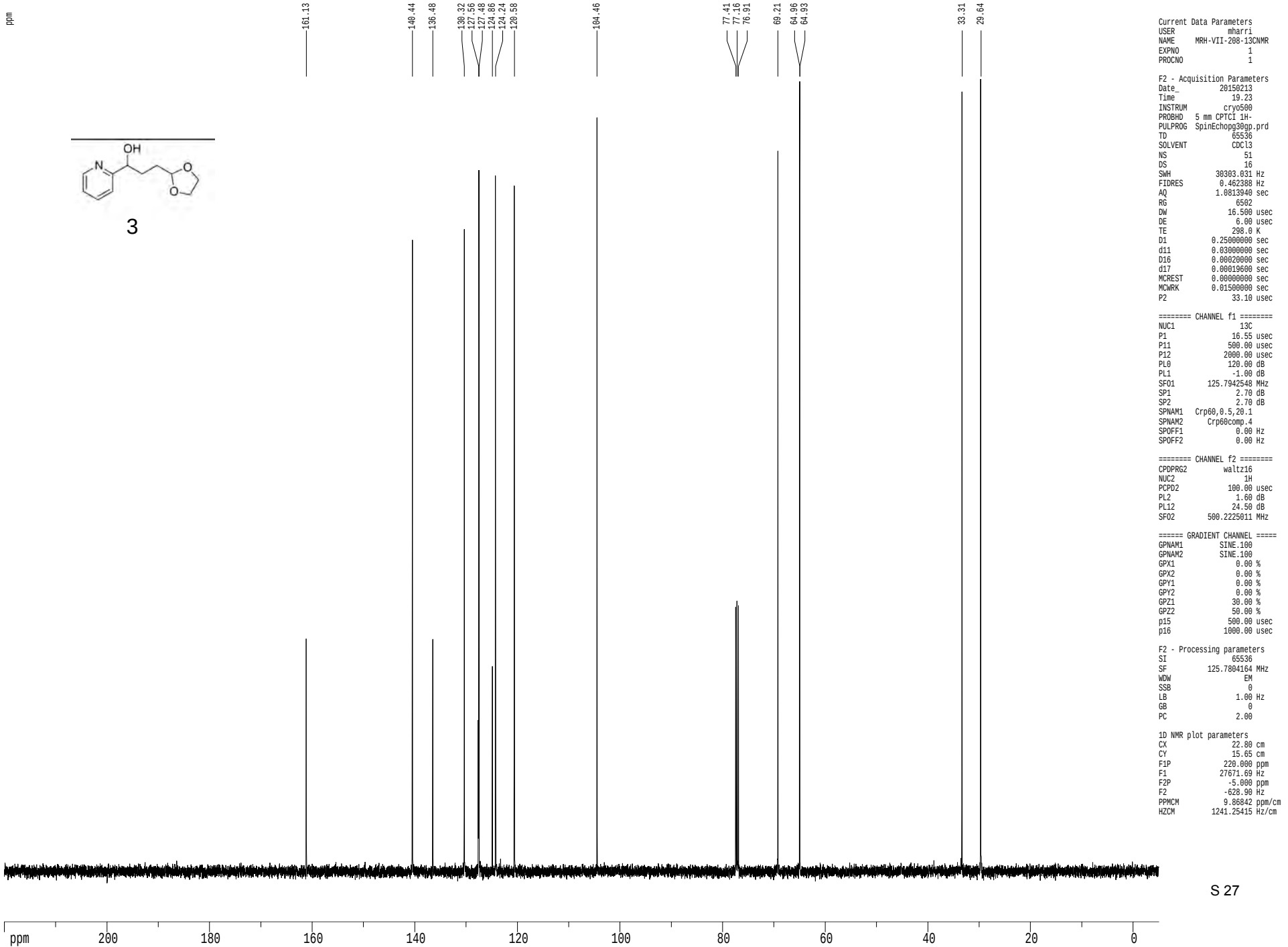
F2 - Acquisition Parameters
Date_            20150213
Time                19.20
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG               zg30
TD                   81728
SOLVENT              CDCl3
NS                       8
DS                       2
SWH              8012.820 Hz
FIDRES           0.098043 Hz
AQ               5.0998774 sec
RG                     6.3
DW                62.400 usec
DE                 6.00 usec
TE                 298.0 K
D1             0.10000000 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                    1H
P1                   7.50 usec
PL1                  1.60 dB
SF01          500.2235015 MHz

F2 - Processing parameters
SI                   65536
SF            500.2200249 MHz
WDW                     EM
SSB                      0
LB                  0.30 Hz
GB                       0
PC                    4.00

1D NMR plot parameters
CX                   22.80 cm
CY                   15.00 cm
F1P                  9.000 ppm
F1                 4501.98 Hz
F2P                 -0.500 ppm
F2                 -250.11 Hz
PPMCM             0.41667 ppm/cm
HZCM            208.42502 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling

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Current Data Parameters
USER              mharri
NAME      MRH-VII-208-13CNMR
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_           20150213
Time               19.23
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                    51
DS                    16
SWH            30303.031 Hz
FIDRES         0.462388 Hz
AQ             1.0813940 sec
RG                  6502
DW                16.500 usec
DE                 6.00 usec
TE                298.0 K
D1             0.25000000 sec
d11            0.03000000 sec
D16            0.00020000 sec
d17            0.00019600 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec
P2                33.10 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                2.70 dB
SP2                2.70 dB
SPNAM1    Crp60,0.5,20.1
SPNAM2       Crp60comp.4
SPOFF1               0.00 Hz
SPOFF2               0.00 Hz

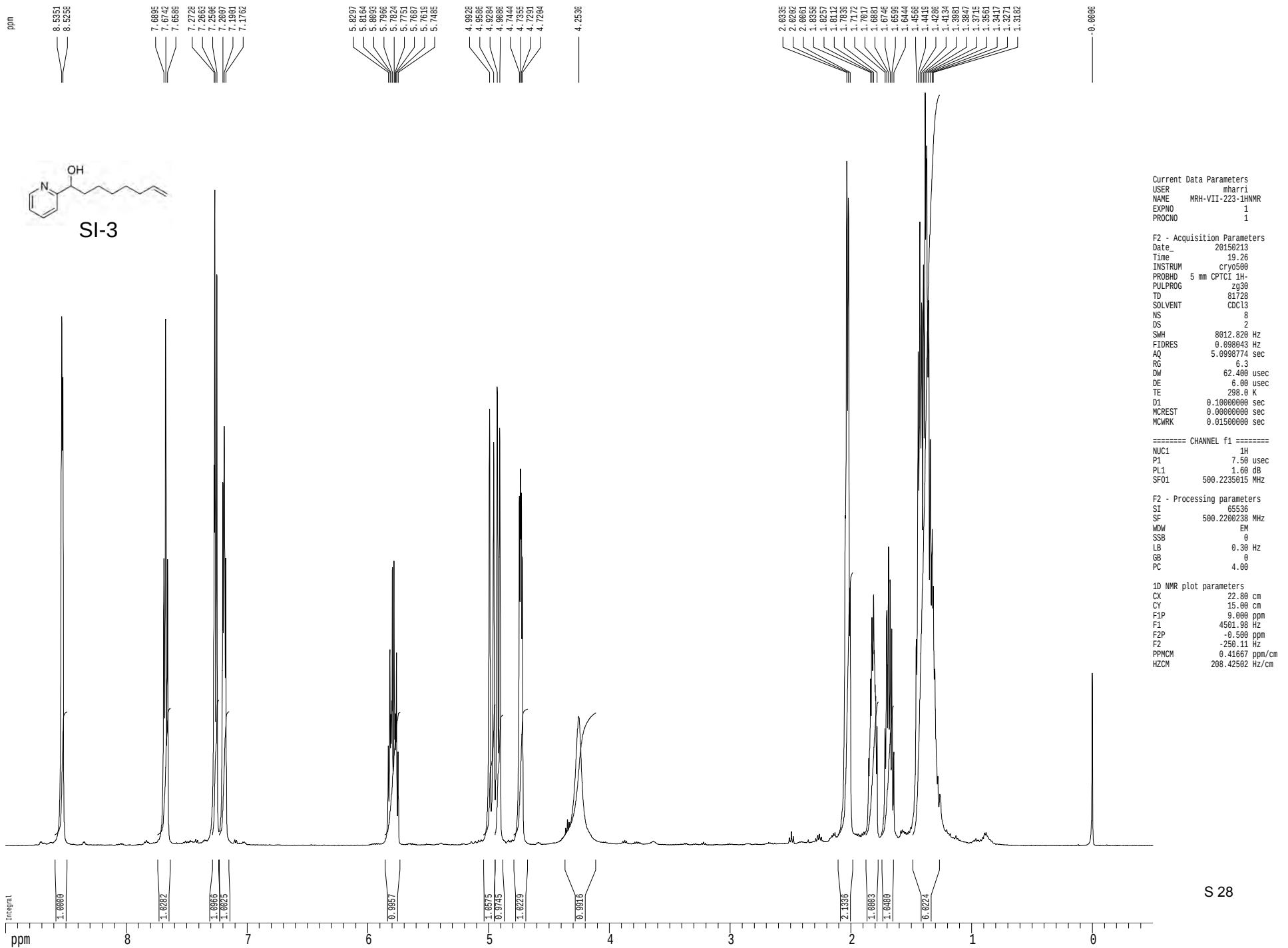
======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2             100.00 usec
PL2                1.60 dB
PL12              24.50 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1          SINE.100
GPNAM2          SINE.100
GPX1                0.00 %
GPX2                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7804164 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 2.00

1D NMR plot parameters
CX                22.80 cm
CY                15.65 cm
F1P             220.000 ppm
F1             27671.69 Hz
F2P              -5.000 ppm
F2              -628.90 Hz
PPMCM           9.86842 ppm/cm
HZCM         1241.25415 Hz/cm
```

1H spectrum



Current Data Parameters
USER mharri
NAME MRH-VII-223-1HNMR
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
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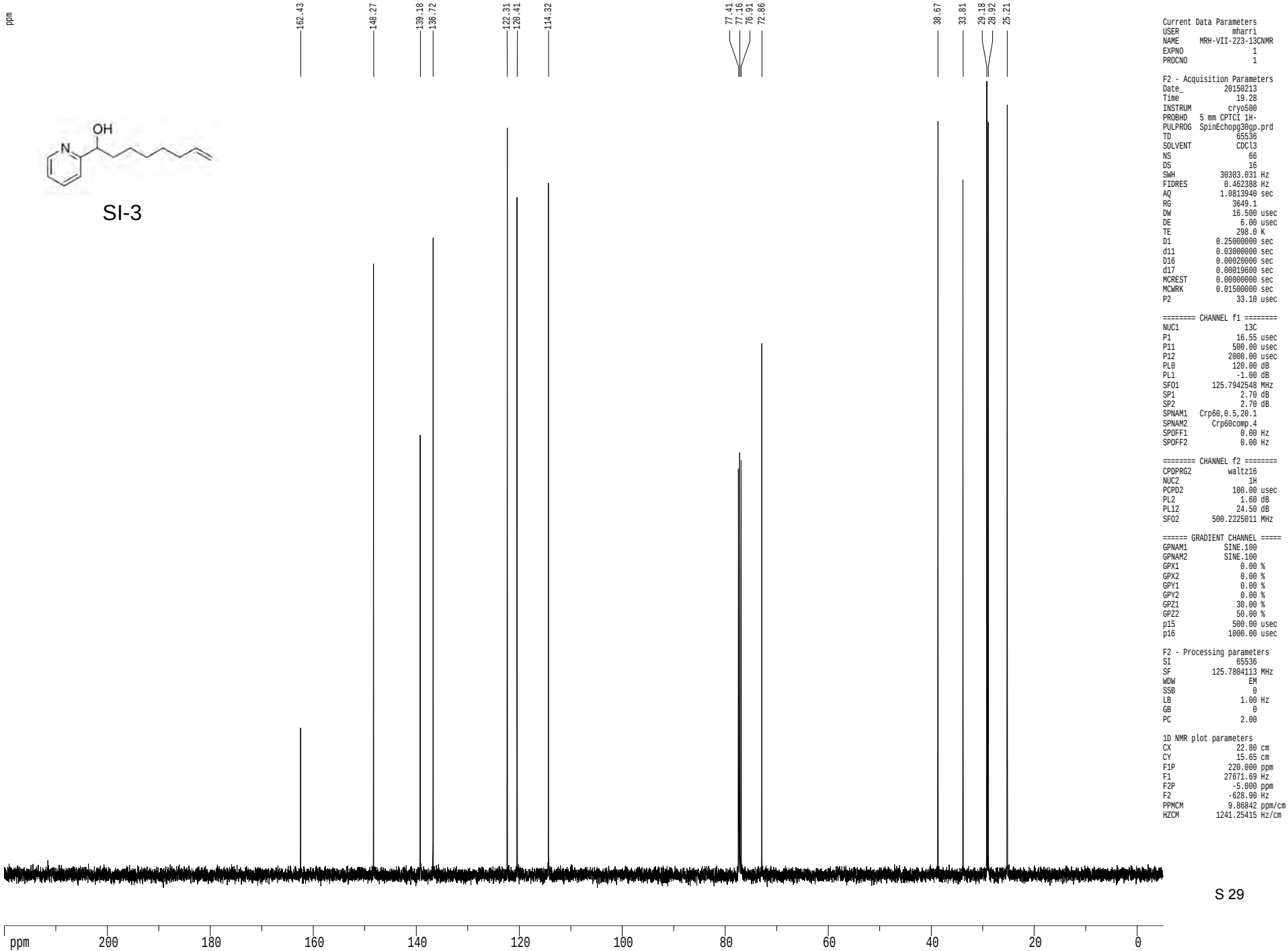
Time 19.26
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG zg30
TD 81728
SOLVENT CDCl3
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 5.0998774 sec
RG 6.3
DW 62.400 usec
DE 6.00 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======== CHANNEL f1 ========
NUC1 1H
P1 7.50 usec
PL1 1.60 dB
SFO1 500.2235015 MHz

F2 - Processing parameters
SI 65536
SF 500.2200238 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 4.00

1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 9.000 ppm
F1 4501.98 Hz
F2P -0.500 ppm
F2 -250.11 Hz
PPMCM 0.41667 ppm/cm
HZCM 208.42502 Hz/cm

Z-restored spin-echo 13C spectrum with 1H decoupling




```
Current Data Parameters
USER                mharri
NAME      MRH-VII-223-13CNMR
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_            20150213
Time                19.28
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                  65536
SOLVENT             CDCl3
NS                     66
DS                     16
SWH             30303.031 Hz
FIDRES          0.462388 Hz
AQ              1.0813940 sec
RG                3649.1
DW                16.500 usec
DE                 6.00 usec
TE                298.0 K
D1             0.25000000 sec
d11            0.03000000 sec
D16            0.00020000 sec
d17            0.00019600 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec
P2                33.10 usec

======== CHANNEL f1 ========
NUC1                  13C
P1                 16.55 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                2.70 dB
SP2                2.70 dB
SPNAM1    Crp60,0.5,20.1
SPNAM2       Crp60comp.4
SPOFF1               0.00 Hz
SPOFF2               0.00 Hz

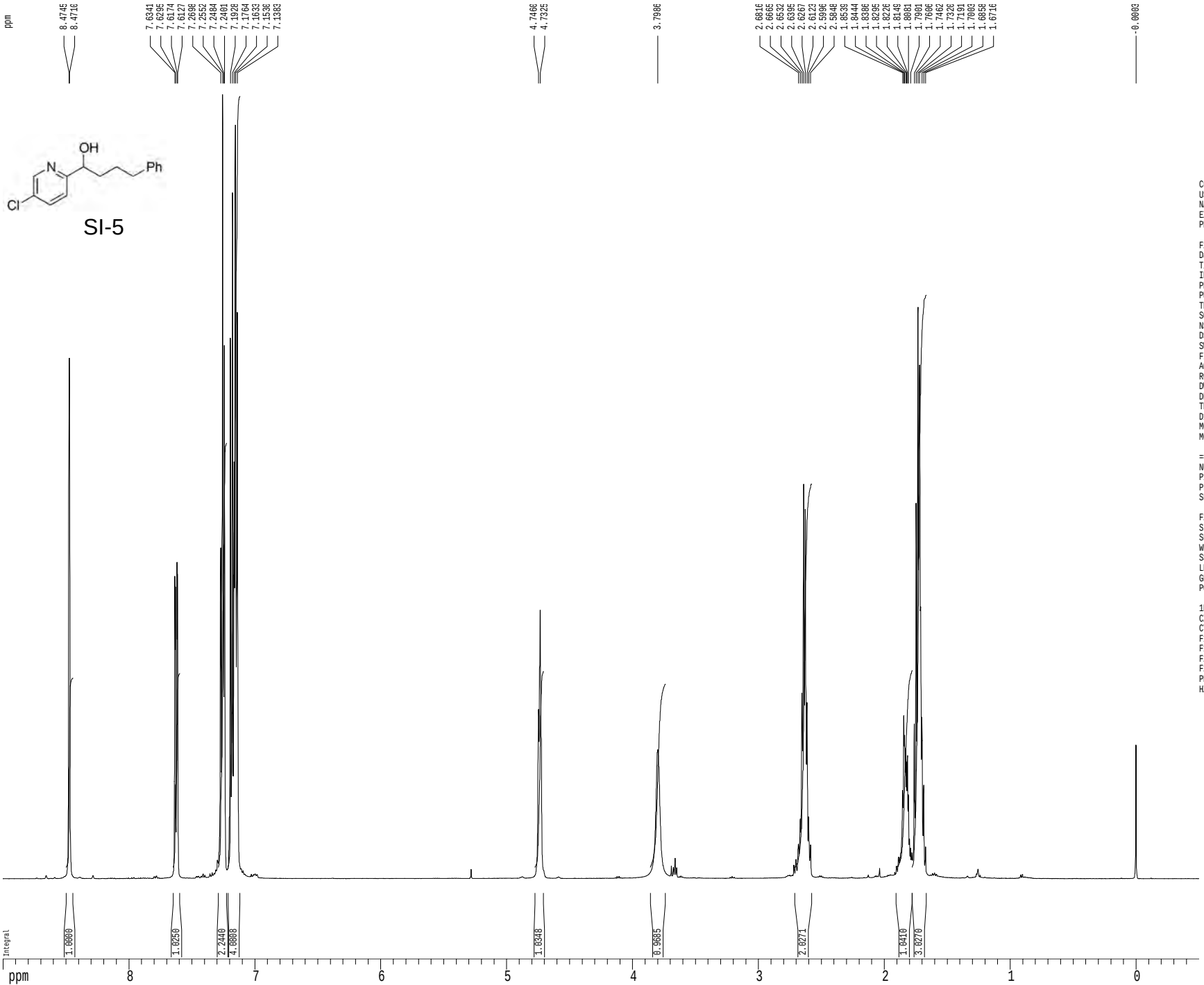
======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                1.60 dB
PL12               24.50 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1           SINE.100
GPNAM2           SINE.100
GPX1                 0.00 %
GPX2                 0.00 %
GPY1                 0.00 %
GPY2                 0.00 %
GPZ1                30.00 %
GPZ2                50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                  65536
SF           125.7804113 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   2.00

1D NMR plot parameters
CX                  22.80 cm
CY                  15.65 cm
F1P               220.000 ppm
F1              27671.69 Hz
F2P                -5.000 ppm
F2               -628.90 Hz
PPMCM             9.86842 ppm/cm
HZCM          1241.25415 Hz/cm
```

1H spectrum



SI-5

```
Current Data Parameters
USER                  mharri
NAME      MRH-VII-269-1HNMR
EXPNO                      1
PROCNO                     1

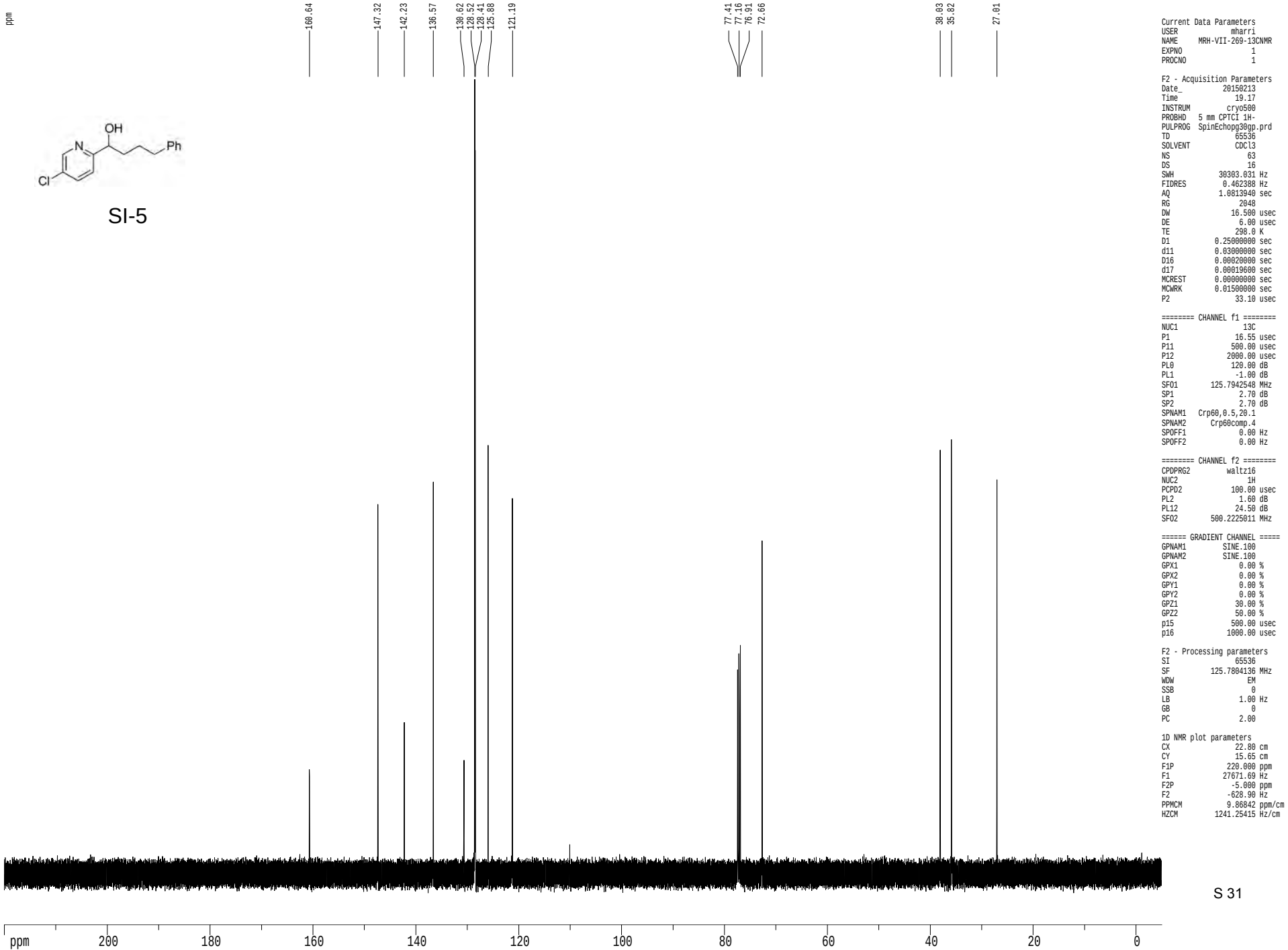
F2 - Acquisition Parameters
Date_              20150213
Time                  19.15
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG                zg30
TD                    81728
SOLVENT             CDCl3T
NS                         8
DS                         2
SWH                8012.820 Hz
FIDRES                0.098043 Hz
AQ                 5.0998774 sec
RG                       6.3
DW                    62.400 usec
DE                     6.00 usec
TE                    298.0 K
D1                 0.10000000 sec
MCREST             0.00000000 sec
MCWRK              0.01500000 sec

======== CHANNEL f1 ========
NUC1                      1H
P1                     7.50 usec
PL1                    1.60 dB
SFO1             500.2235015 MHz

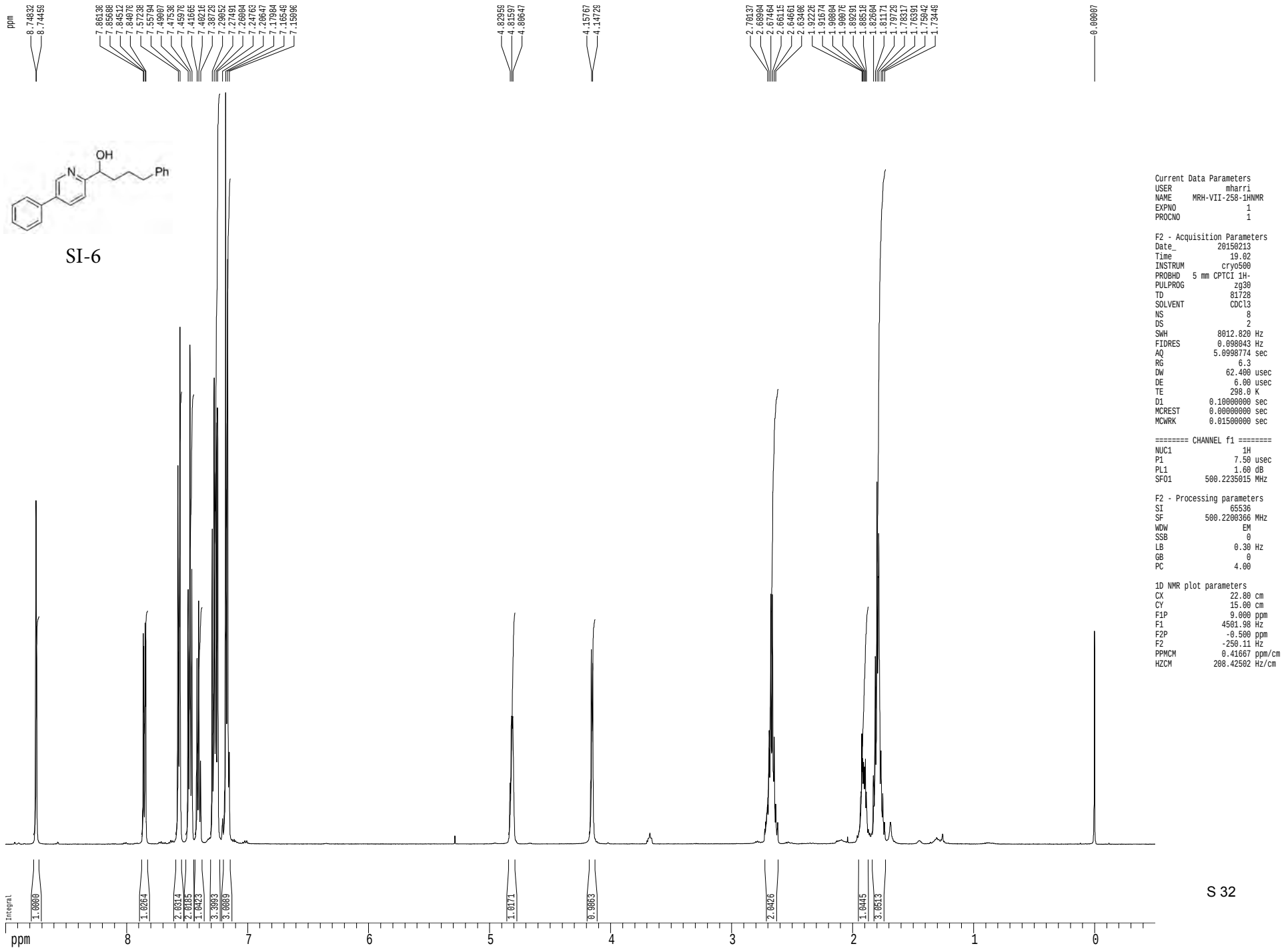
F2 - Processing parameters
SI                        65536
SF                 500.2200365 MHz
WDW                        EM
SSB                        0
LB                     0.30 Hz
GB                         0
PC                     4.00

1D NMR plot parameters
CX                    22.80 cm
CY                    15.00 cm
F1P                    9.000 ppm
F1                  4501.98 Hz
F2P                   -0.500 ppm
F2                  -250.11 Hz
PPMCM                 0.41667 ppm/cm
HZCM                208.42502 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



1H spectrum



SI-6

```
Current Data Parameters
USER                mharri
NAME      MRH-VII-258-1HNMR
EXPNO                    1
PROCNO                   1

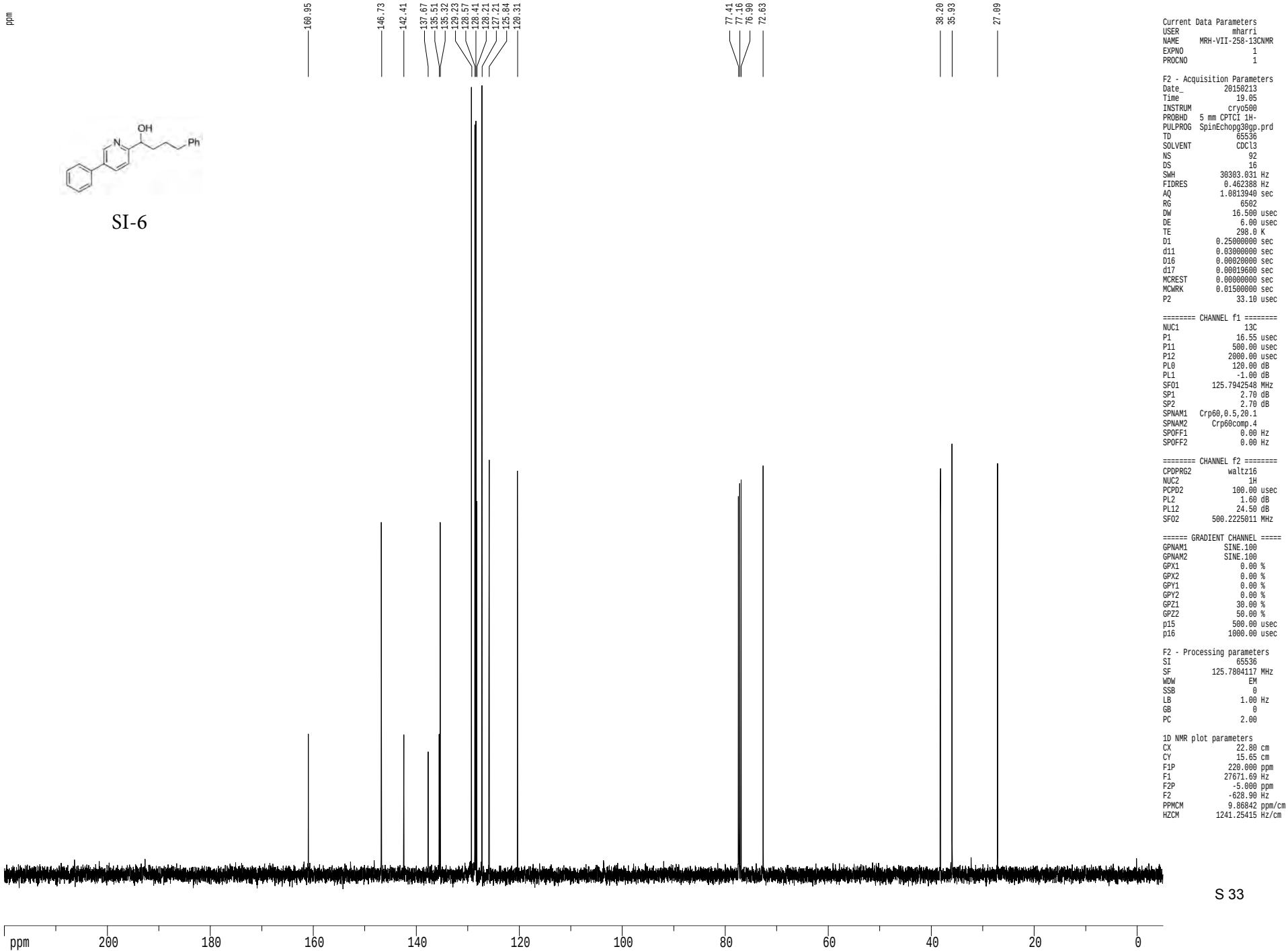
F2 - Acquisition Parameters
Date_            20150213
Time                19.02
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG               zg30
TD                   81728
SOLVENT              CDCl3
NS                       8
DS                       2
SWH              8012.820 Hz
FIDRES           0.098043 Hz
AQ               5.0998774 sec
RG                     6.3
DW                62.400 usec
DE                 6.00 usec
TE                 298.0 K
D1             0.10000000 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                    1H
P1                   7.50 usec
PL1                  1.60 dB
SFO1          500.2235015 MHz

F2 - Processing parameters
SI                    65536
SF            500.2200366 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    4.00

1D NMR plot parameters
CX                   22.80 cm
CY                   15.00 cm
F1P                   9.000 ppm
F1                 4501.98 Hz
F2P                  -0.500 ppm
F2                 -250.11 Hz
PPMCM             0.41667 ppm/cm
HZCM            208.42502 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



SI-6

```
Current Data Parameters
USER                mharri
NAME      MRH-VII-258-13CNMR
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_            20150213
Time                19.05
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                  65536
SOLVENT             CDCl3
NS                     92
DS                     16
SWH             30303.031 Hz
FIDRES          0.462388 Hz
AQ              1.0813940 sec
RG                   6502
DW                 16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1              0.25000000 sec
d11             0.03000000 sec
D16             0.00020000 sec
d17             0.00019600 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec
P2                  33.10 usec

======== CHANNEL f1 ========
NUC1                   13C
P1                  16.55 usec
P11                500.00 usec
P12               2000.00 usec
PL0                120.00 dB
PL1                 -1.00 dB
SFO1          125.7942548 MHz
SP1                  2.70 dB
SP2                  2.70 dB
SPNAM1    Crp60,0.5,20.1
SPNAM2       Crp60comp.4
SPOFF1               0.00 Hz
SPOFF2               0.00 Hz

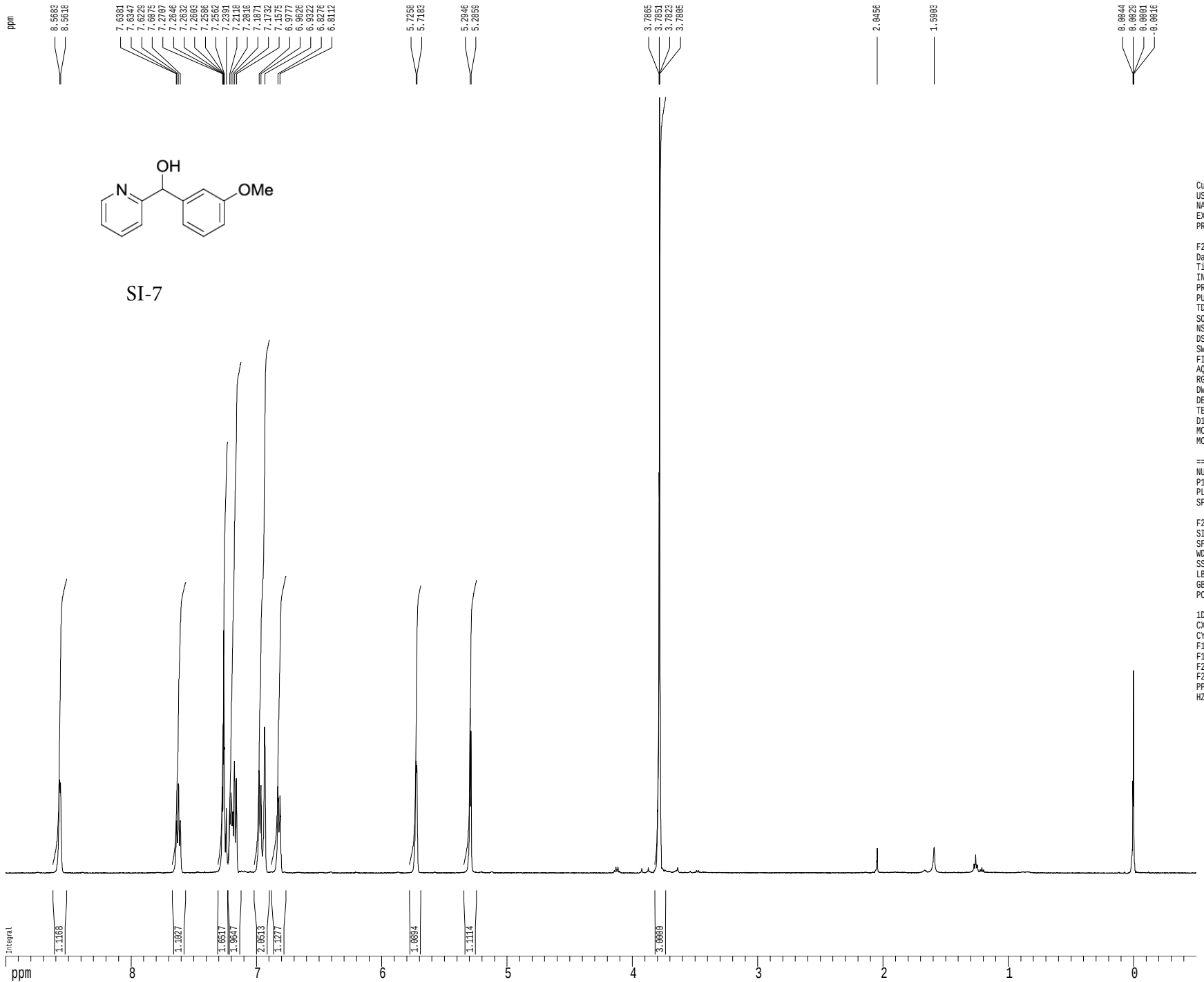
======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2              100.00 usec
PL2                  1.60 dB
PL12                24.50 dB
SFO2          500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1           SINE.100
GPNAM2           SINE.100
GPX1                 0.00 %
GPX2                 0.00 %
GPY1                 0.00 %
GPY2                 0.00 %
GPZ1                30.00 %
GPZ2                50.00 %
p15                500.00 usec
p16               1000.00 usec

F2 - Processing parameters
SI                   65536
SF            125.7804117 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   2.00

1D NMR plot parameters
CX                  22.80 cm
CY                  15.65 cm
F1P               220.000 ppm
F1              27671.69 Hz
F2P                -5.000 ppm
F2               -628.90 Hz
PPMCM             9.86842 ppm/cm
HZCM           1241.25415 Hz/cm
```

1H spectrum



SI-7

```
Current Data Parameters
USER              lhanna
NAME       LEH-5-037-H1
EXPNO                1
PROCNO               1

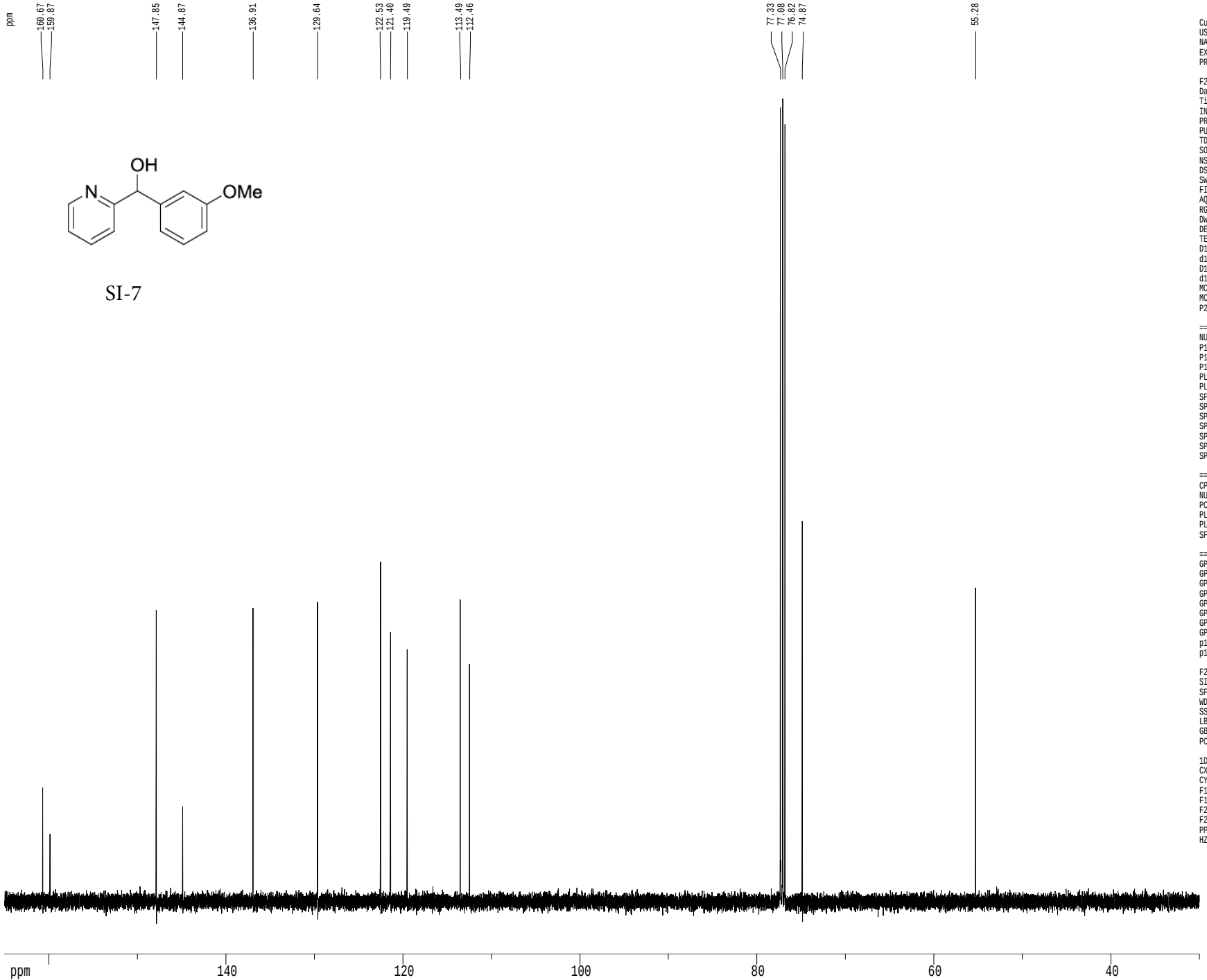
F2 - Acquisition Parameters
Date_          20150114
Time              18.24
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG            zg30
TD                32048
SOLVENT            CDCl3
NS                    8
DS                    2
SWH            8012.820 Hz
FIDRES         0.250026 Hz
AQ             1.9998451 sec
RG                  5.7
DW                62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                1H
P1                7.50 usec
PL1               1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                65536
SF           500.2200314 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 4.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P                9.000 ppm
F1              4501.98 Hz
F2P               -0.500 ppm
F2              -250.11 Hz
PPMCM          0.41667 ppm/cm
HZCM         208.42502 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



SI-7

```
Current Data Parameters
USER                lhanna
NAME          LEH-5-037-C13
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20150114
Time                 18.28
INSTRUM             cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                   65536
SOLVENT              CDCl3
NS                     513
DS                      16
SWH              30303.031 Hz
FIDRES           0.462388 Hz
AQ               1.0813940 sec
RG                  7298.2
DW                 16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1              0.25000000 sec
d11             0.03000000 sec
D16             0.00020000 sec
d17             0.00019600 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec
P2                  33.10 usec

======== CHANNEL f1 ========
NUC1                   13C
P1                  16.55 usec
P11                500.00 usec
P12               2000.00 usec
PL0                120.00 dB
PL1                 -1.00 dB
SFO1          125.7942548 MHz
SP1                  2.70 dB
SP2                  2.70 dB
SPNAM1    Crp60,0.5,20.1
SPNAM2       Crp60comp.4
SPOFF1               0.00 Hz
SPOFF2               0.00 Hz

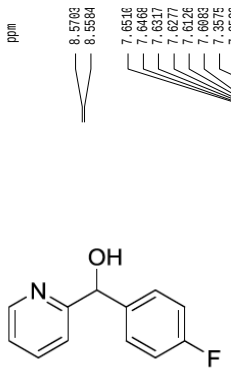
======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2              100.00 usec
PL2                  1.60 dB
PL12                24.50 dB
SFO2          500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1           SINE.100
GPNAM2           SINE.100
GPX1                 0.00 %
GPX2                 0.00 %
GPY1                 0.00 %
GPY2                 0.00 %
GPZ1                30.00 %
GPZ2                50.00 %
p15                500.00 usec
p16               1000.00 usec

F2 - Processing parameters
SI                   65536
SF            125.7804190 MHz
WDW                     no
SSB                      0
LB                   0.00 Hz
GB                       0
PC                   2.00

1D NMR plot parameters
CX                  22.80 cm
CY                  15.65 cm
F1P               165.000 ppm
F1              20753.77 Hz
F2P                30.000 ppm
F2              3773.41 Hz
PPMCM             5.92105 ppm/cm
HZCM            744.75250 Hz/cm
```

1H spectrum



SI-8

Current Data Parameters
USER lhanna
NAME LEH-5-149-2
EXPNO 1
PROCNO 1

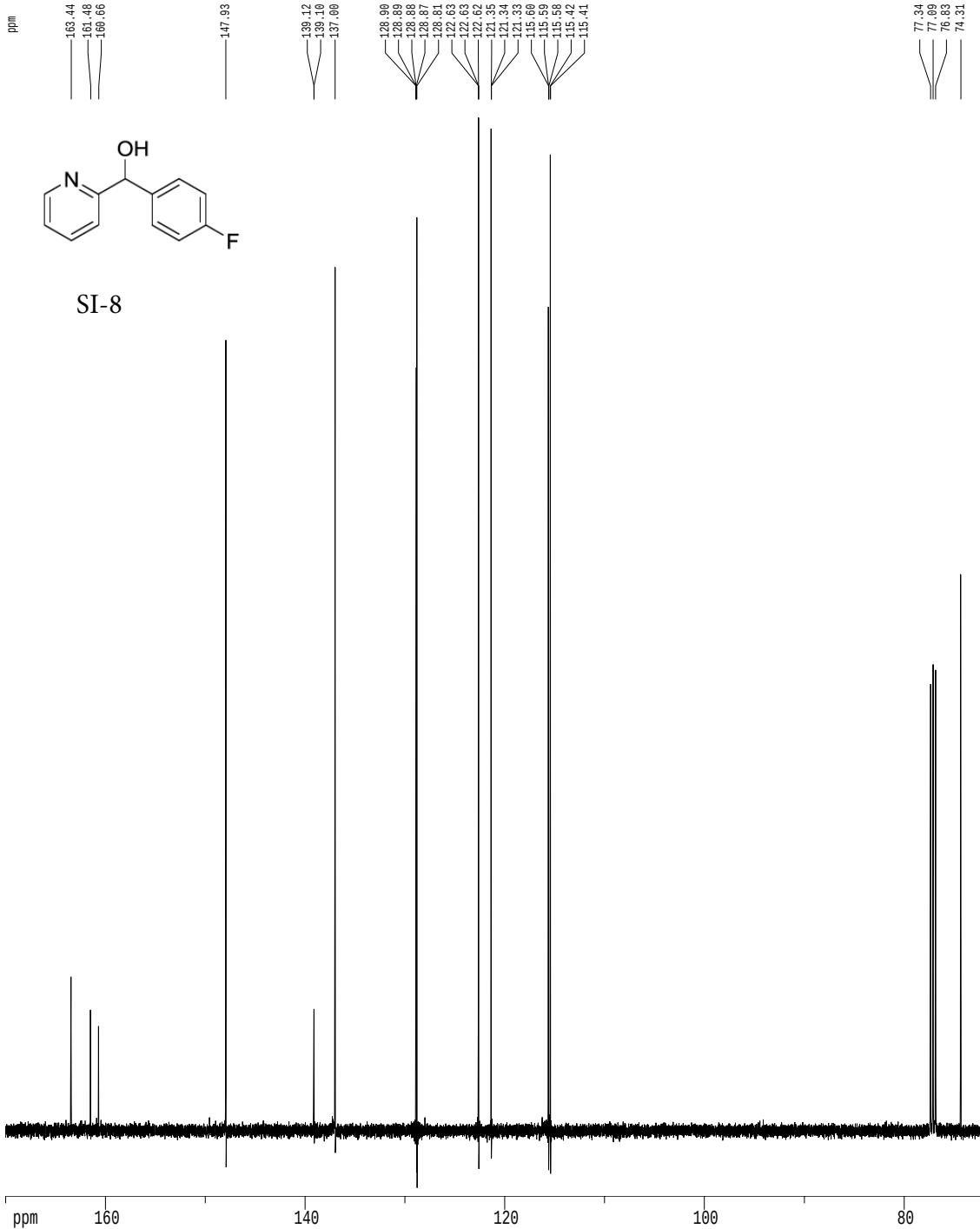
F2 - Acquisition Parameters
Date_ 20150320
Time 13.41
INSTRUM drx400
PROBHD 5 mm QNP H/F/P
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 6410.256 Hz
FIDRES 0.097813 Hz
AQ 5.1118579 sec
RG 287.4
DW 78.000 usec
DE 4.50 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 0.00 dB
SFO1 400.1328009 MHz

F2 - Processing parameters
SI 65536
SF 400.1300211 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 9.000 ppm
F1 3601.17 Hz
F2P -0.500 ppm
F2 -200.06 Hz
PPMCM 0.41667 ppm/cm
HZCM 166.72086 Hz/cm

Z-restored spin-echo 13C spectrum with 1H decoupling



Current Data Parameters
USER lhanna
NAME LEH-5-149-c13
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20150320
Time 14.42
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG SpinEchopg30gp.prd
TD 65536
SOLVENT CDCl3
NS 594
DS 16
SWH 30303.031 Hz
FIDRES 0.462388 Hz
AQ 1.0813940 sec
RG 7298.2
DW 16.500 usec
DE 6.00 usec
TE 298.0 K
D1 0.25000000 sec
d11 0.03000000 sec
D16 0.00020000 sec
d17 0.00019600 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
P2 33.10 usec

======== CHANNEL f1 ========
NUC1 13C
P1 16.55 usec
P11 500.00 usec
P12 2000.00 usec
PL0 120.00 dB
PL1 -1.00 dB
SFO1 125.7942548 MHz
SP1 2.70 dB
SP2 2.70 dB
SPNAM1 Crp60,0.5,20.1
SPNAM2 Crp60comp.4
SPOFF1 0.00 Hz
SPOFF2 0.00 Hz

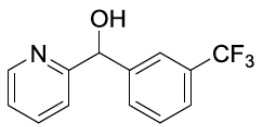
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 1.60 dB
PL12 24.50 dB
SFO2 500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1 SINE.100
GPNAM2 SINE.100
GPX1 0.00 %
GPX2 0.00 %
GPY1 0.00 %
GPY2 0.00 %
GPZ1 30.00 %
GPZ2 50.00 %
p15 500.00 usec
p16 1000.00 usec

F2 - Processing parameters
SI 65536
SF 125.7804190 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.80 cm
CY 15.65 cm
F1P 170.000 ppm
F1 21382.67 Hz
F2P 20.000 ppm
F2 2515.61 Hz
PPMCM 6.57895 ppm/cm
HZCM 827.50281 Hz/cm

1H spectrum



SI-9


```
Current Data Parameters
USER              lhanna
NAME       LEH-5-067-H1
EXPNO                1
PROCNO               1

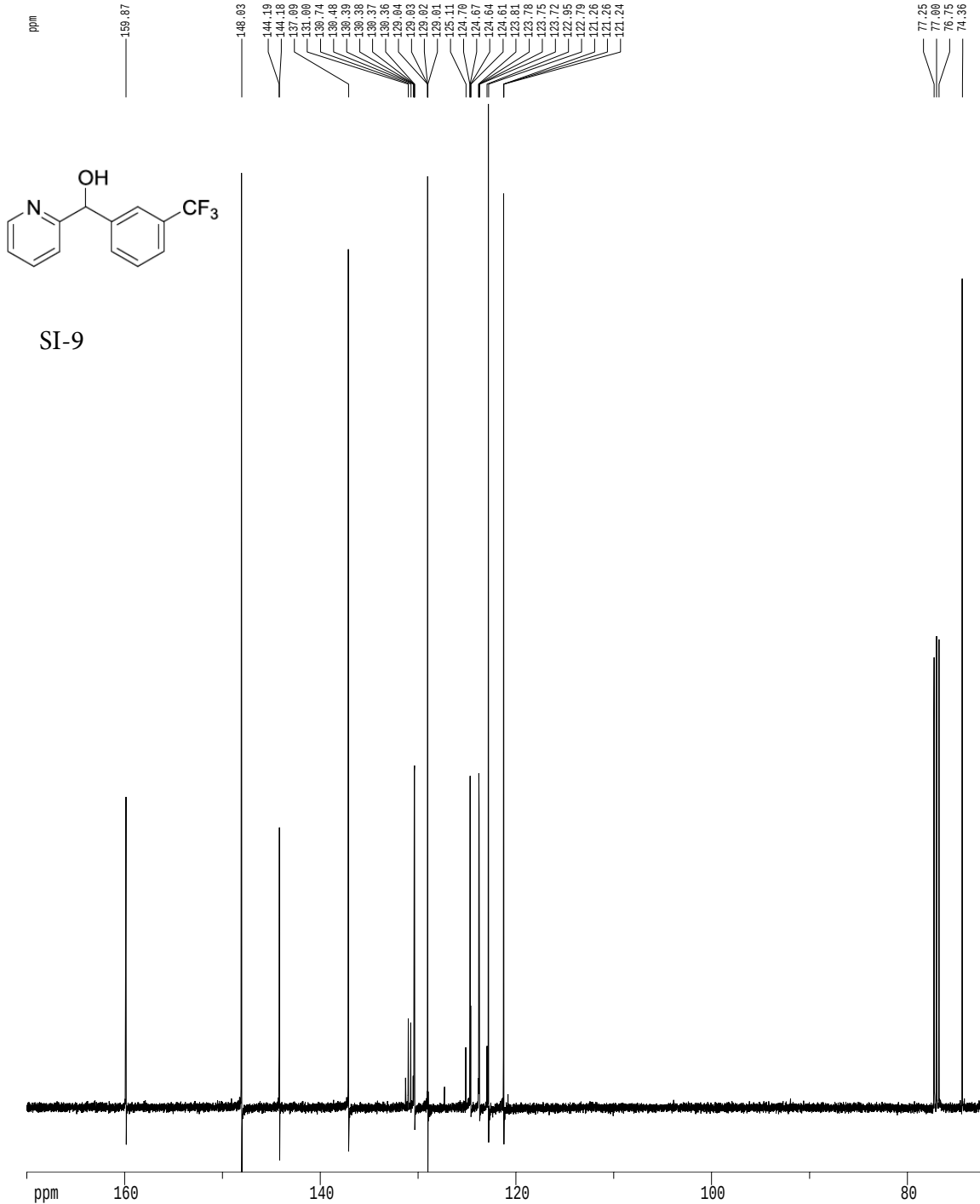
F2 - Acquisition Parameters
Date_          20150122
Time              18.35
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 32048
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES             0.250026 Hz
AQ              1.9998451 sec
RG                  10.1
DW                 62.400 usec
DE                  6.00 usec
TE                298.0 K
D1             0.10000000 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                  65536
SF           500.2200315 MHz
WDW                    no
SSB                     0
LB                  0.00 Hz
GB                      0
PC                  4.00

1D NMR plot parameters
CX                  22.80 cm
CY                  15.00 cm
F1P                 9.000 ppm
F1                4501.98 Hz
F2P                -0.500 ppm
F2                -250.11 Hz
PPMCM            0.41667 ppm/cm
HZCM           208.42502 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



SI-9

```
Current Data Parameters
USER                lhanna
NAME          LEH-5-067-C13
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20150122
Time                18.41
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                  65536
SOLVENT             CDCl3
NS                    771
DS                     16
SWH             30303.031 Hz
FIDRES          0.462388 Hz
AQ              1.0813940 sec
RG                11585.2
DW                16.500 usec
DE                 6.00 usec
TE                298.0 K
D1             0.25000000 sec
d11            0.03000000 sec
D16            0.00020000 sec
d17            0.00019600 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec
P2                33.10 usec

======== CHANNEL f1 ========
NUC1                  13C
P1                 16.55 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                2.70 dB
SP2                2.70 dB
SPNAM1    Crp60,0.5,20.1
SPNAM2       Crp60comp.4
SPOFF1               0.00 Hz
SPOFF2               0.00 Hz

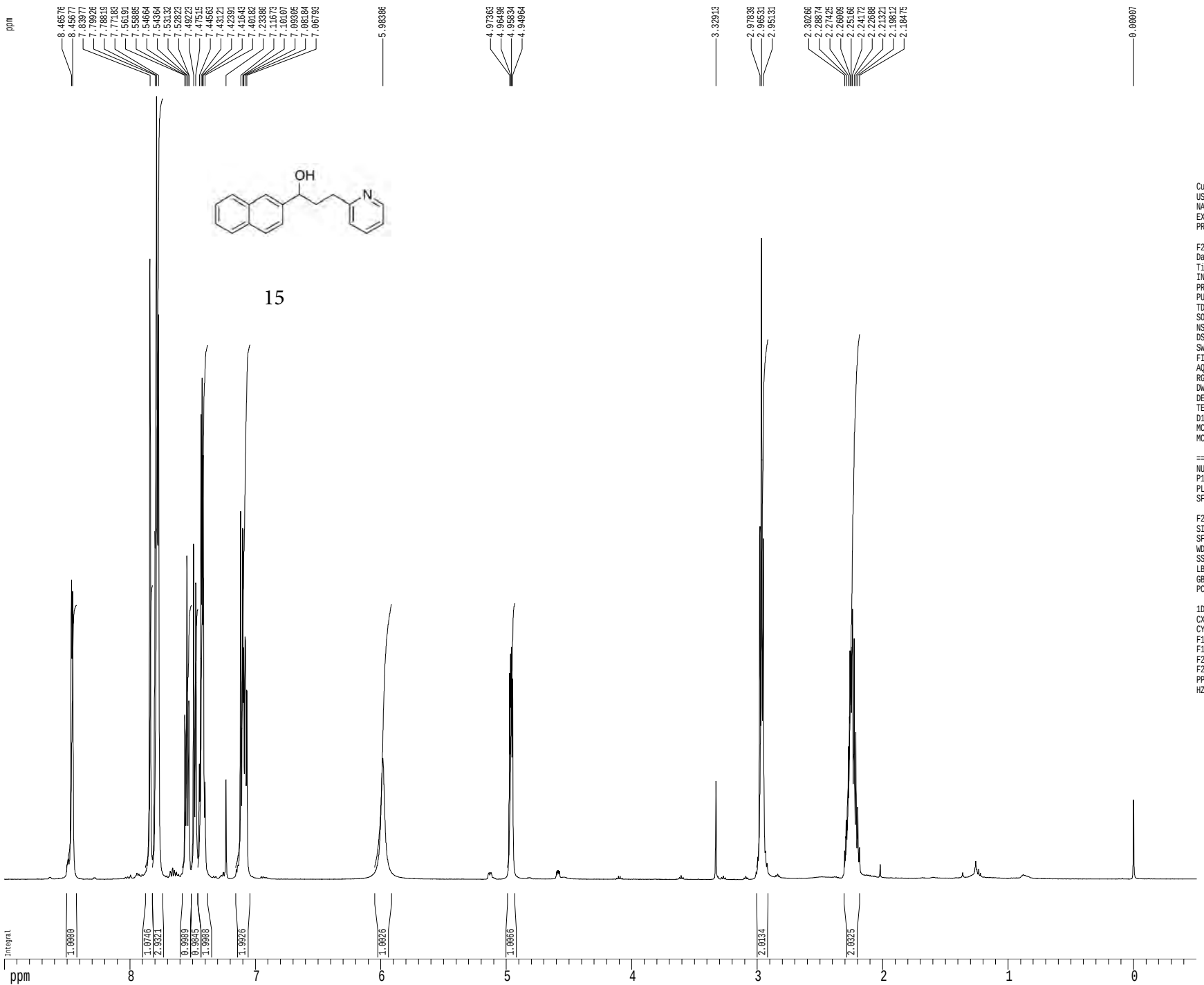
======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                1.60 dB
PL12              24.50 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1          SINE.100
GPNAM2          SINE.100
GPX1                0.00 %
GPX2                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                  65536
SF           125.7804295 MHz
WDW                    no
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   2.00

1D NMR plot parameters
CX                  22.80 cm
CY                  15.65 cm
F1P               170.000 ppm
F1               21382.67 Hz
F2P                20.000 ppm
F2                2515.61 Hz
PPMCM             6.57895 ppm/cm
HZCM            827.50281 Hz/cm
```

1H spectrum




```
Current Data Parameters
USER                mharri
NAME      MRH-VII-236-1HNMR
EXPNO                    2
PROCNO                   1

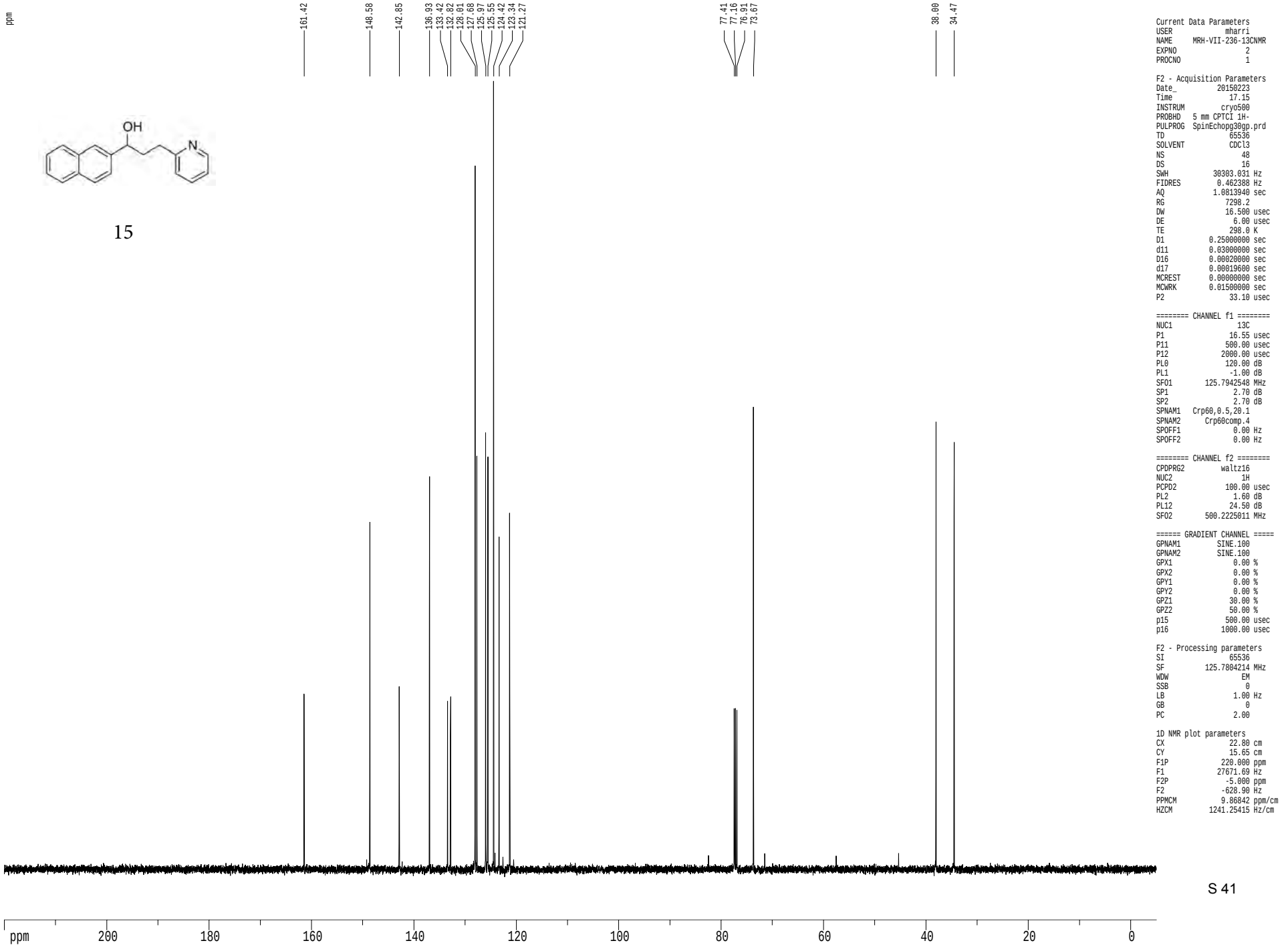
F2 - Acquisition Parameters
Date_            20150223
Time                17.13
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG               zg30
TD                   81728
SOLVENT              CDCl3
NS                       8
DS                       2
SWH              8012.820 Hz
FIDRES           0.098043 Hz
AQ               5.0998774 sec
RG                       5
DW                 62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1              0.10000000 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec

======== CHANNEL f1 ========
NUC1                    1H
P1                   7.50 usec
PL1                  1.60 dB
SFO1          500.2235015 MHz

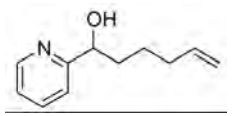
F2 - Processing parameters
SI                   65536
SF            500.2200448 MHz
WDW                     EM
SSB                      0
LB                  0.30 Hz
GB                       0
PC                   4.00

1D NMR plot parameters
CX                  22.80 cm
CY                  15.00 cm
F1P                 9.000 ppm
F1                4501.98 Hz
F2P                -0.500 ppm
F2                 -250.11 Hz
PPMCM            0.41667 ppm/cm
HZCM           208.42502 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



1H spectrum



SI-10

```
Current Data Parameters
USER                mharri
NAME      MRH-VII-212-1HNMR
EXPNO                    1
PROCNO                   1

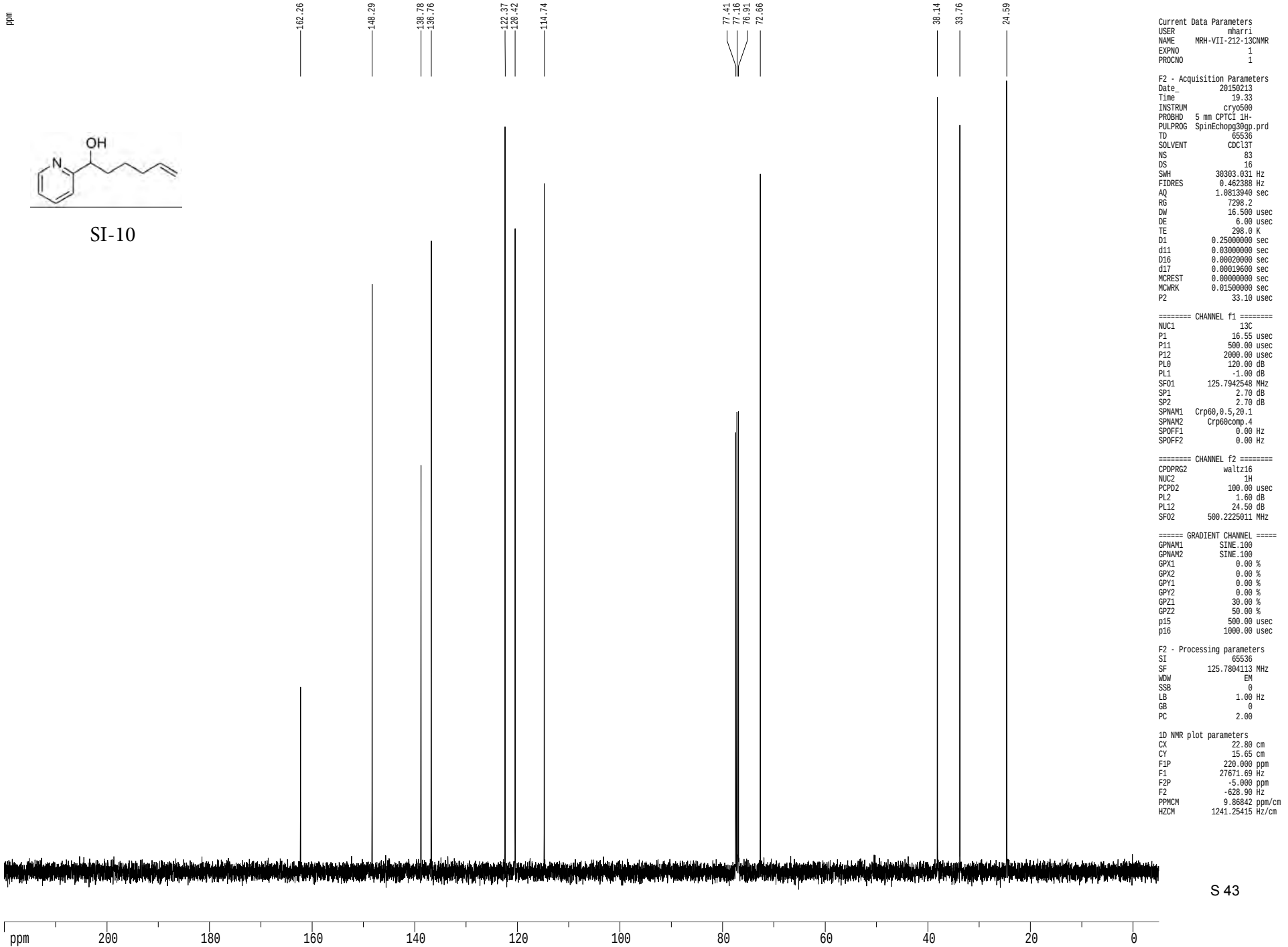
F2 - Acquisition Parameters
Date_            20150213
Time                19.31
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG              zg30
TD                  81728
SOLVENT             CDCl3
NS                      8
DS                      2
SWH              8012.820 Hz
FIDRES           0.098043 Hz
AQ               5.0998774 sec
RG                      9
DW                 62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1              0.10000000 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec

======== CHANNEL f1 ========
NUC1                    1H
P1                   7.50 usec
PL1                  1.60 dB
SF01          500.2235015 MHz

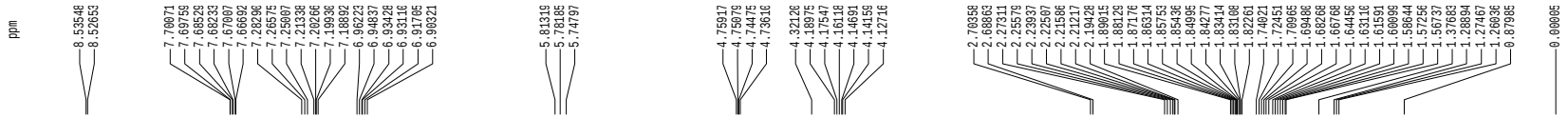
F2 - Processing parameters
SI                   65536
SF            500.2200264 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    4.00

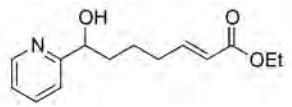
1D NMR plot parameters
CX                   22.80 cm
CY                   15.00 cm
F1P                   9.000 ppm
F1                 4501.98 Hz
F2P                  -0.500 ppm
F2                 -250.11 Hz
PPMCM             0.41667 ppm/cm
HZCM            208.42502 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



1H spectrum





24


```
Current Data Parameters
USER              mharri
NAME      MRH-VII-260-1HNMR
EXPNO                  1
PROCNO                 1

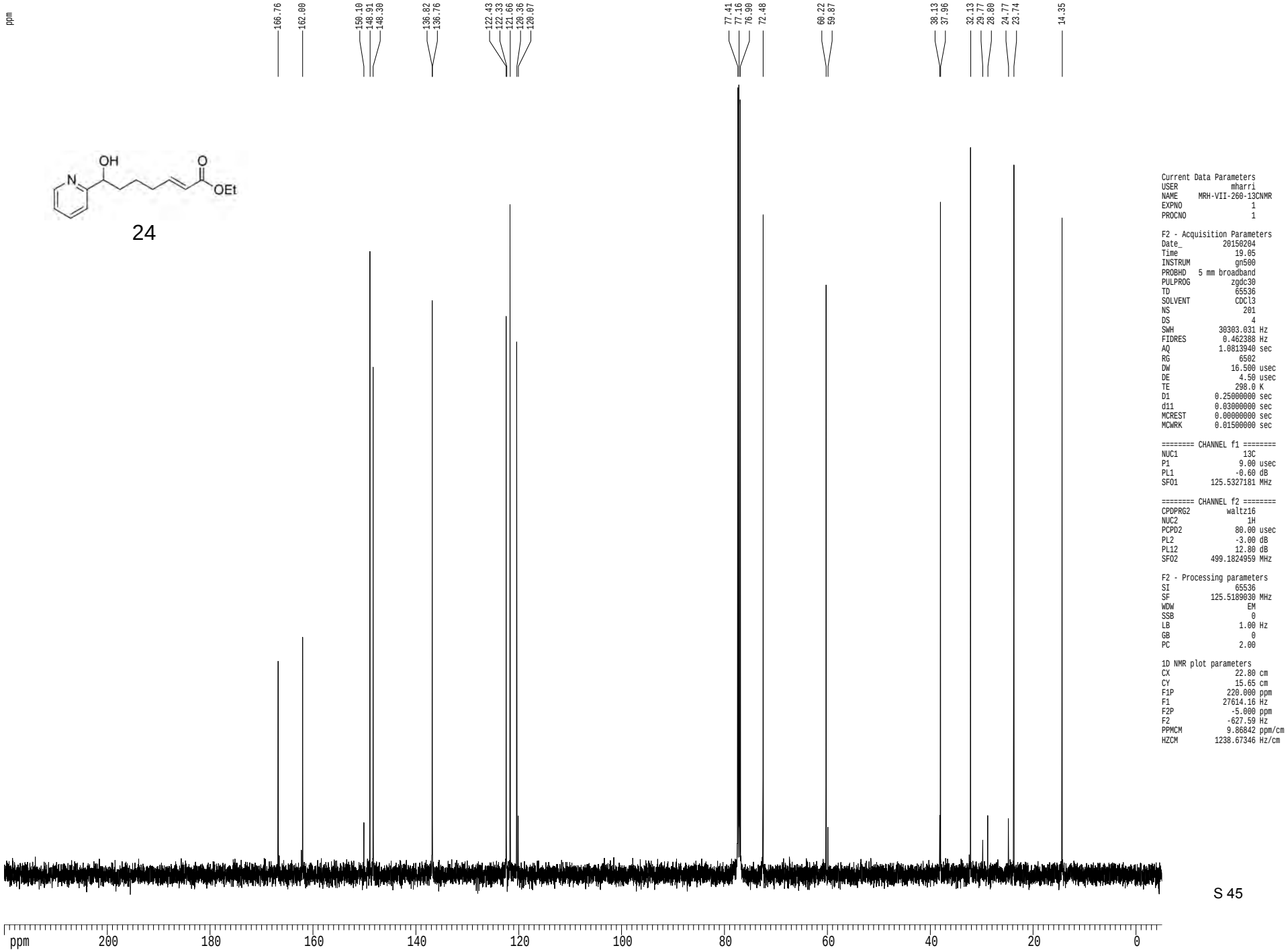
F2 - Acquisition Parameters
Date_           20150204
Time               19.01
INSTRUM            gn500
PROBHD   5 mm broadband
PULPROG             zg30
TD                 81728
SOLVENT           CDCl3T
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.098043 Hz
AQ              5.0998774 sec
RG                    64
DW                62.400 usec
DE                 6.00 usec
TE                298.0 K
D1             0.10000000 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 12.00 usec
PL1                -5.80 dB
SFO1         499.1834943 MHz

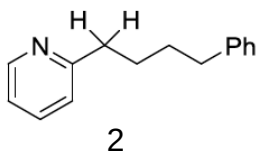
F2 - Processing parameters
SI                 65536
SF           499.1800153 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                9.000 ppm
F1               4492.62 Hz
F2P               -0.500 ppm
F2               -249.59 Hz
PPMCM           0.41667 ppm/cm
HZCM          207.99168 Hz/cm
```

13C spectrum with 1H decoupling



1H spectrum



2

```
Current Data Parameters
USER              lhanna
NAME      LEH-5-054-c1-f007
EXPNO                  1
PROCNO                 1

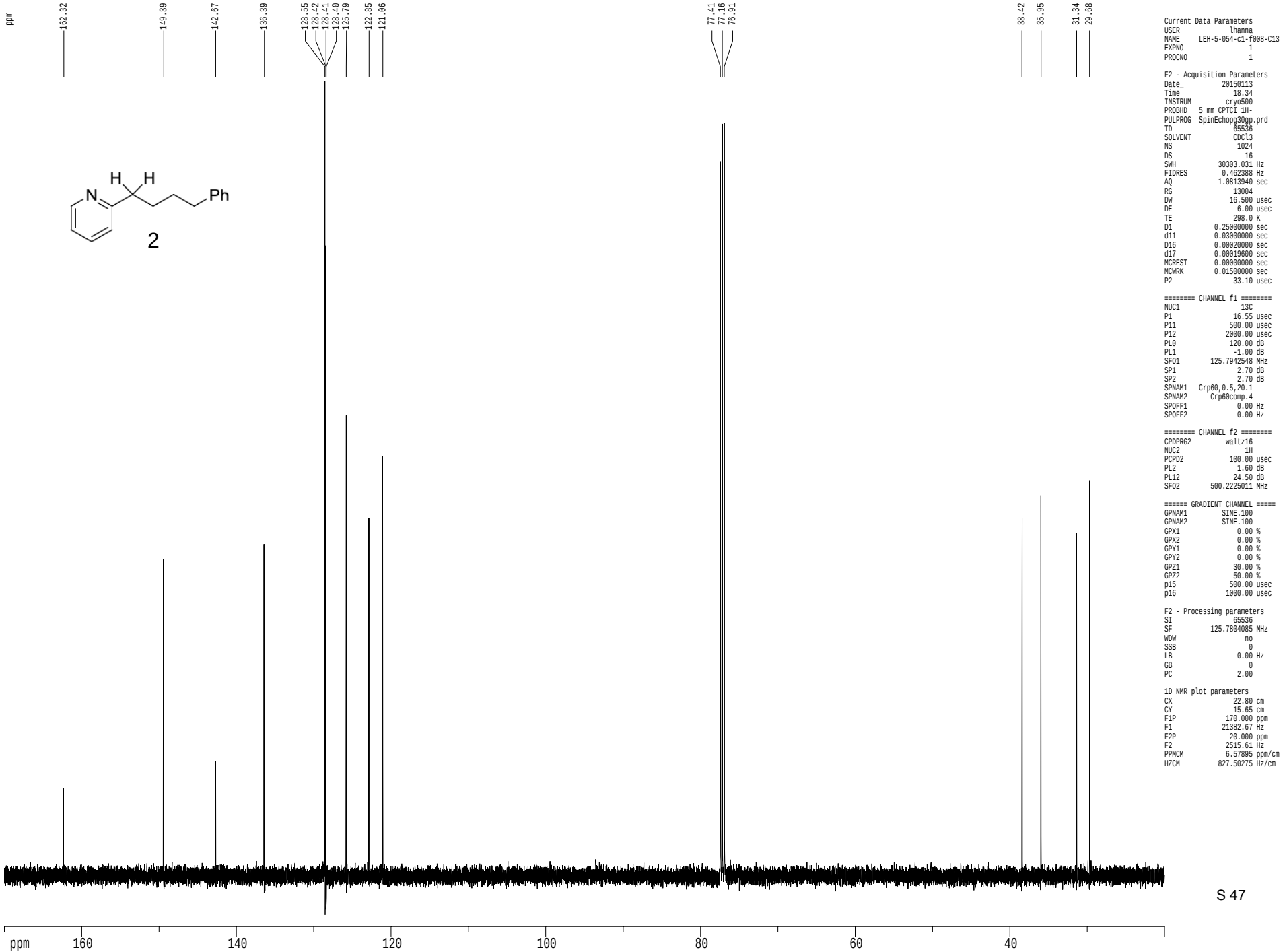
F2 - Acquisition Parameters
Date_           20150114
Time              20.33
INSTRUM          drx400
PROBHD   5 mm QNP H/F/P
PULPROG            zg30
TD                25640
SOLVENT           CDCl3
NS                    8
DS                    2
SWH            6410.256 Hz
FIDRES          0.250010 Hz
AQ             1.9999700 sec
RG                406.4
DW               78.000 usec
DE                4.50 usec
TE                298.0 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                12.00 usec
PL1                0.00 dB
SFO1        400.1328009 MHz

F2 - Processing parameters
SI                 65536
SF          400.1300216 MHz
WDW                   no
SSB                    0
LB                0.00 Hz
GB                     0
PC                2.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P               9.000 ppm
F1              3601.17 Hz
F2P              -0.500 ppm
F2              -200.06 Hz
PPMCM           0.41667 ppm/cm
HZCM          166.72086 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



Current Data Parameters
USER lhanna
NAME LEH-5-054-c1-f008-C13
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20150113
Time 18.34
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG SpinEchopg30gp.prd
TD 65536
SOLVENT CDCl3
NS 1024
DS 16
SWH 30303.031 Hz
FIDRES 0.462398 Hz
AQ 1.0813940 sec
RG 13004
DW 16.500 usec
DE 6.00 usec
TE 298.0 K
D1 0.25000000 sec
d11 0.03000000 sec
D16 0.00020000 sec
d17 0.00019600 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
P2 33.10 usec

======== CHANNEL f1 ========
NUC1 13C
P1 16.55 usec
P11 500.00 usec
P12 2000.00 usec
PL0 120.00 dB
PL1 -1.00 dB
SFO1 125.7942548 MHz
SP1 2.70 dB
SP2 2.70 dB
SPNAM1 Crp60,0.5,20.1
SPNAM2 Crp60comp.4
SPOFF1 0.00 Hz
SPOFF2 0.00 Hz

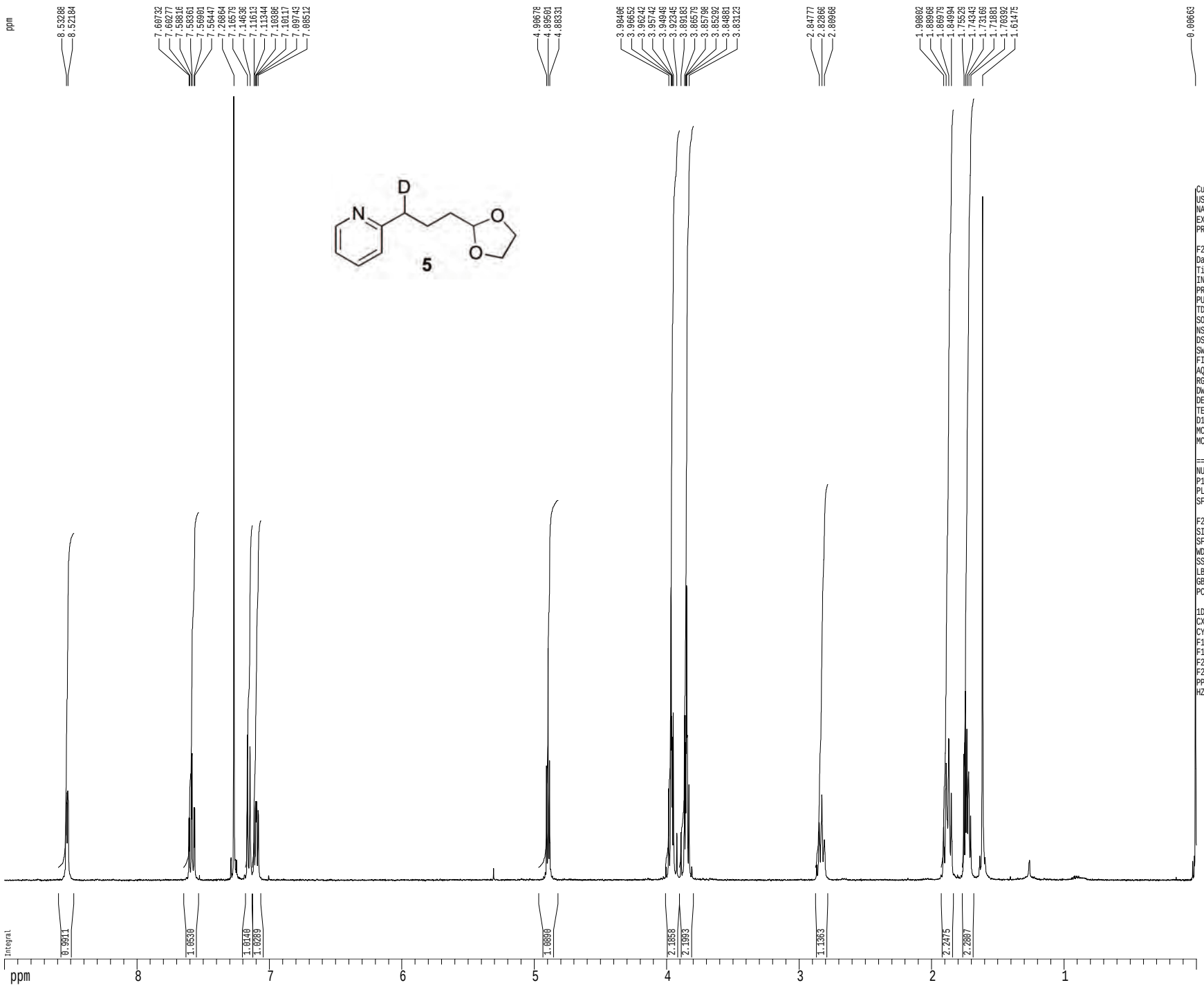
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 1.60 dB
PL12 24.50 dB
SFO2 500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1 SINE.100
GPNAM2 SINE.100
GPX1 0.00 %
GPX2 0.00 %
GPY1 0.00 %
GPY2 0.00 %
GPZ1 30.00 %
GPZ2 50.00 %
p15 500.00 usec
p16 1000.00 usec

F2 - Processing parameters
SI 65536
SF 125.7804085 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.80 cm
CY 15.65 cm
F1P 170.000 ppm
F1 21382.67 Hz
F2P 20.000 ppm
F2 2515.61 Hz
PPMCM 6.57895 ppm/cm
HZCM 827.50275 Hz/cm

1H spectrum



Current Data Parameters

USER	lhanna
NAME	LEH-5-044-c3-f021
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20150113
Time	13.46
INSTRUM	drx400
PROBHD	5 mm QNP H/F/P
PULPROG	zg30
TD	25640
SOLVENT	CDCl3
NS	16
DS	2
SWH	6410.256 Hz
FIDRES	0.250010 Hz
AQ	1.9999700 sec
RG	1024
DW	78.000 usec
DE	4.50 usec
TE	298.0 K
D1	0.10000000 sec
MCREST	0.00000000 sec
MCWRK	0.01500000 sec

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

NUC1	1H
P1	12.00 usec
PL1	0.00 dB
SFO1	400.1328009 MHz

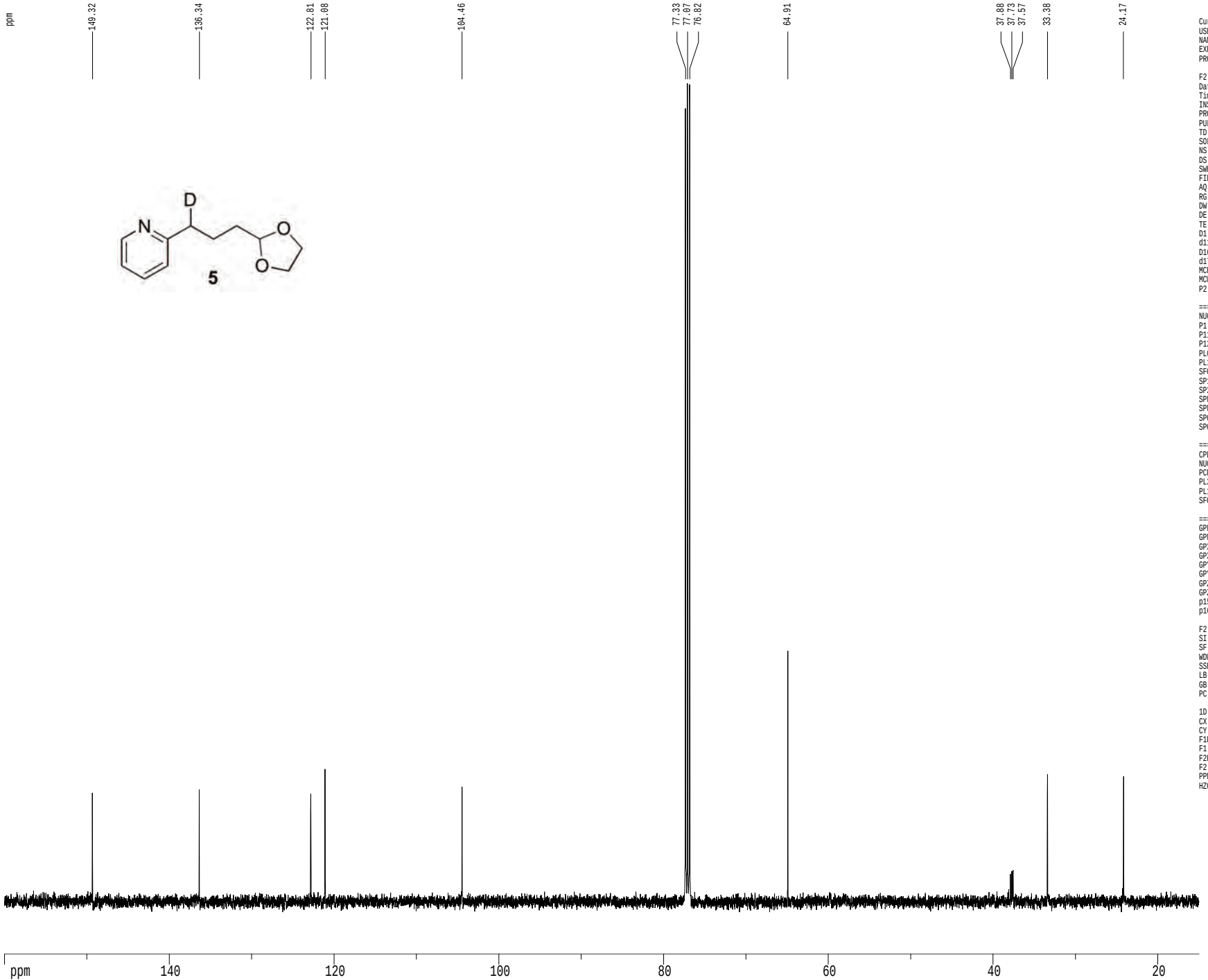
F2 - Processing parameters

SI	65536
SF	400.1300175 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	2.00

1D NMR plot parameters

CX	22.80 cm
CY	15.00 cm
F1P	9.000 ppm
F1	3601.17 Hz
F2P	0.000 ppm
F2	0.00 Hz
PPMCM	0.39474 ppm/cm
HZCM	157.94606 Hz/cm

Z-restored spin-echo 13C spectrum with 1H decoupling




```
Current Data Parameters
USER                lhanna
NAME      LEH-5-044-c3-f020-C13
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_            20150113
Time                12.24
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                  65536
SOLVENT             CDCl3
NS                   1024
DS                     16
SWH             30303.031 Hz
FIDRES          0.462398 Hz
AQ              1.0813940 sec
RG                  13004
DW                16.500 usec
DE                 6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec
P2                33.10 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                2.70 dB
SP2                2.70 dB
SPNAM1   Crp60,0.5,20.1
SPNAM2      Crp60comp.4
SPOFF1               0.00 Hz
SPOFF2               0.00 Hz

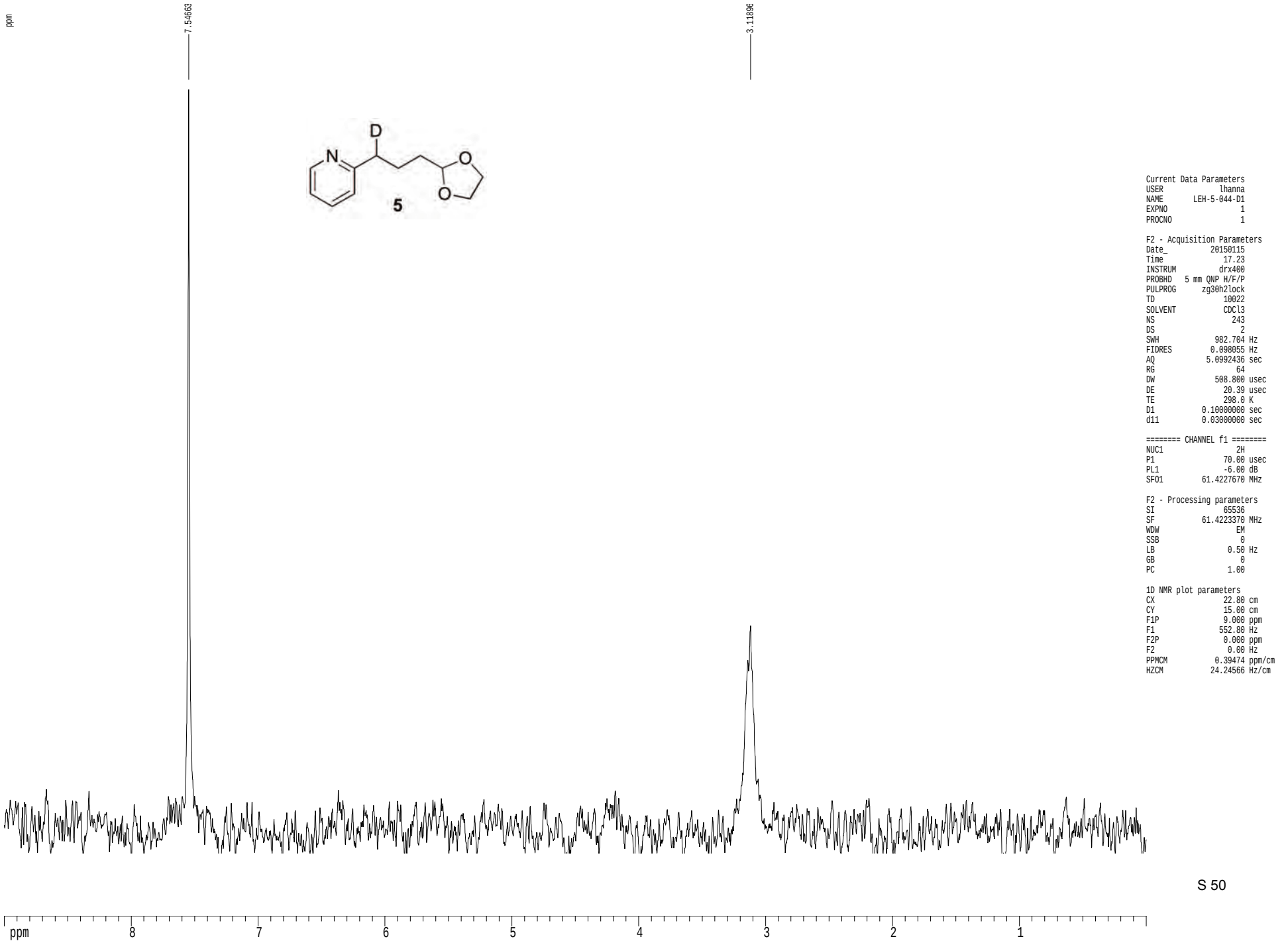
======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2             100.00 usec
PL2                1.60 dB
PL12              24.50 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1          SINE.100
GPNAM2          SINE.100
GPX1                0.00 %
GPX2                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                  65536
SF           125.7804190 MHz
WDW                    EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.65 cm
F1P              160.000 ppm
F1             20124.87 Hz
F2P               15.000 ppm
F2              1886.71 Hz
PPMCM           6.35965 ppm/cm
HZCM          799.91937 Hz/cm
```

2H spectrum (measure via lock channel without changing any cables)




```
Current Data Parameters
USER              lhanna
NAME        LEH-5-044-D1
EXPNO                1
PROCNO               1

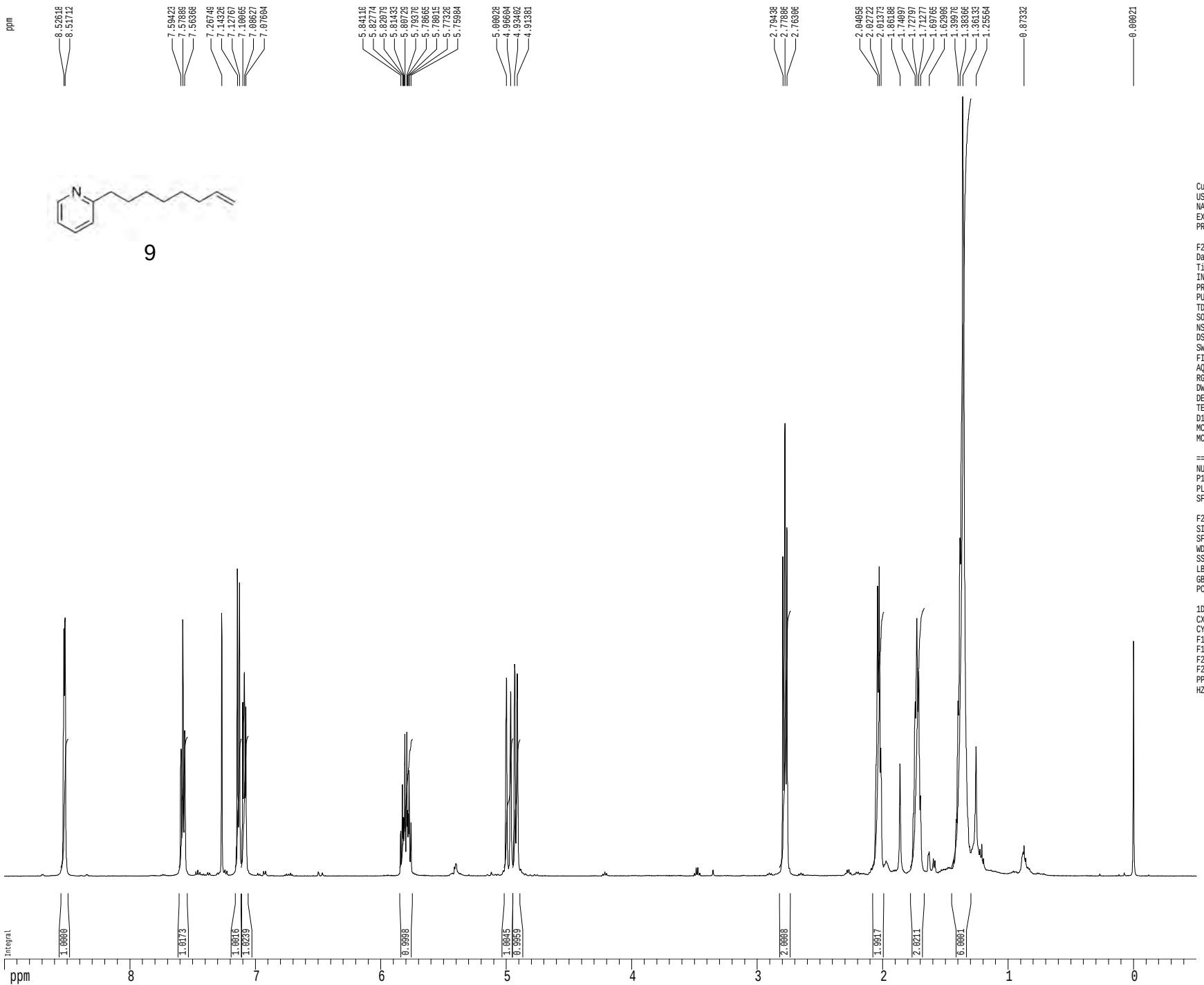
F2 - Acquisition Parameters
Date_          20150115
Time              17.23
INSTRUM          drx400
PROBHD   5 mm QNP H/F/P
PULPROG       zg30h2lock
TD                10022
SOLVENT           CDCl3
NS                  243
DS                    2
SWH             982.704 Hz
FIDRES        0.098055 Hz
AQ           5.0992436 sec
RG                   64
DW              508.800 usec
DE               20.39 usec
TE               298.0 K
D1           0.10000000 sec
d11          0.03000000 sec

======== CHANNEL f1 ========
NUC1                 2H
P1                70.00 usec
PL1               -6.00 dB
SFO1         61.4227670 MHz

F2 - Processing parameters
SI                  65536
SF           61.4223370 MHz
WDW                    EM
SSB                     0
LB                 0.50 Hz
GB                      0
PC                 1.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                9.000 ppm
F1               552.80 Hz
F2P                0.000 ppm
F2                 0.00 Hz
PPMCM           0.39474 ppm/cm
HZCM           24.24566 Hz/cm
```

1H spectrum




```
Current Data Parameters
USER                mharri
NAME      MRH-VII-232-1HNMR
EXPNO                    1
PROCNO                   1

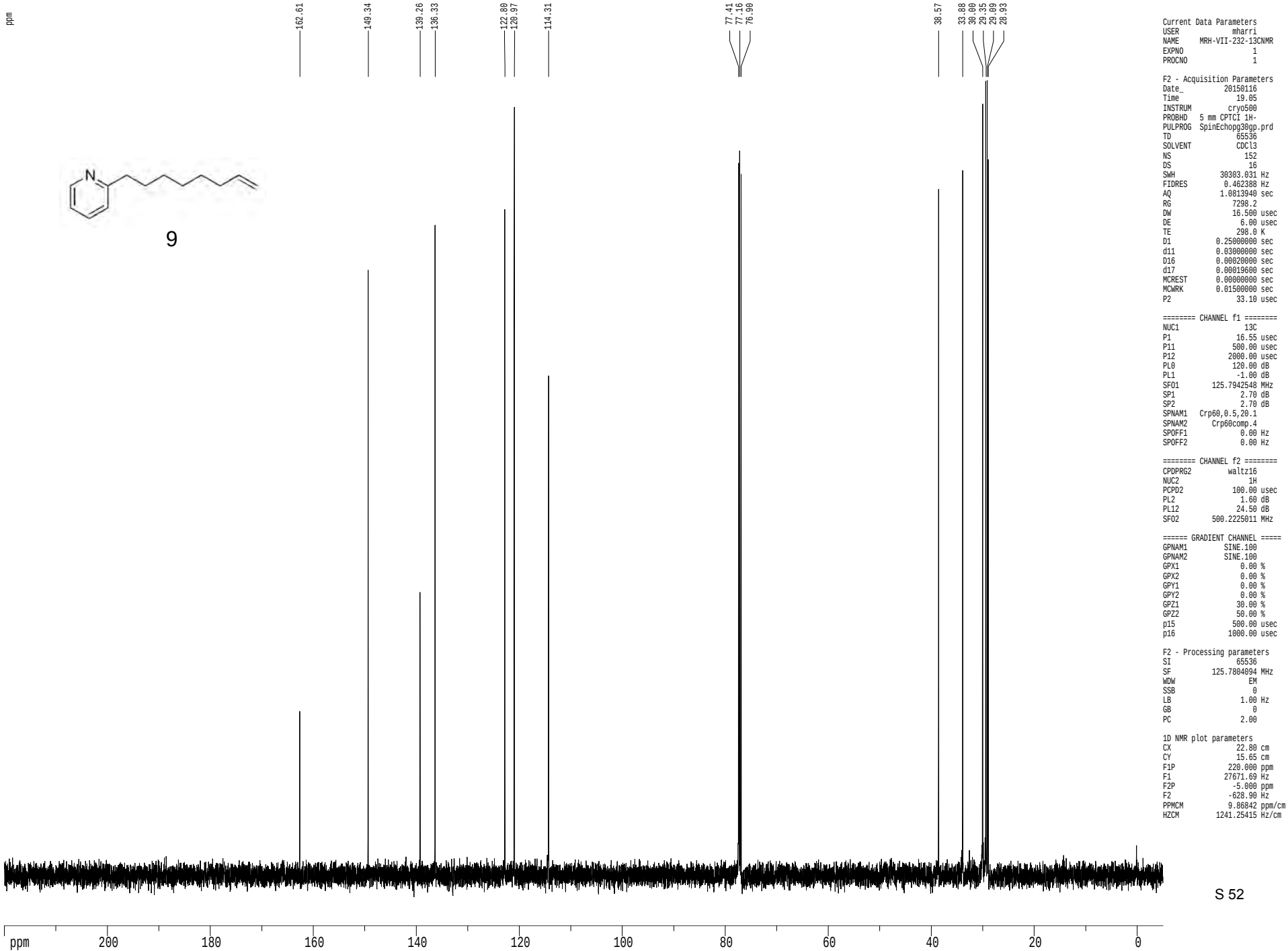
F2 - Acquisition Parameters
Date_            20150116
Time                19.00
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 81728
SOLVENT            CDCl3
NS                     8
DS                     2
SWH              8012.820 Hz
FIDRES           0.098043 Hz
AQ               5.0998774 sec
RG                   4.5
DW                62.400 usec
DE                 6.00 usec
TE                298.0 K
D1             0.10000000 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 7.50 usec
PL1                1.60 dB
SF01         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200280 MHz
WDW                   EM
SSB                    0
LB                 0.30 Hz
GB                     0
PC                 4.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P                9.000 ppm
F1              4501.98 Hz
F2P               -0.500 ppm
F2              -250.11 Hz
PPMCM           0.41667 ppm/cm
HZCM          208.42502 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling




```
Current Data Parameters
USER              mharri
NAME      MRH-VII-232-13CNMR
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_           20150116
Time              19.05
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT           CDCl3
NS                  152
DS                   16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ             1.0813940 sec
RG                7298.2
DW                16.500 usec
DE                 6.00 usec
TE                298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec
P2                33.10 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                16.55 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1               2.70 dB
SP2               2.70 dB
SPNAM1   Crp60,0.5,20.1
SPNAM2      Crp60comp.4
SPOFF1               0.00 Hz
SPOFF2               0.00 Hz

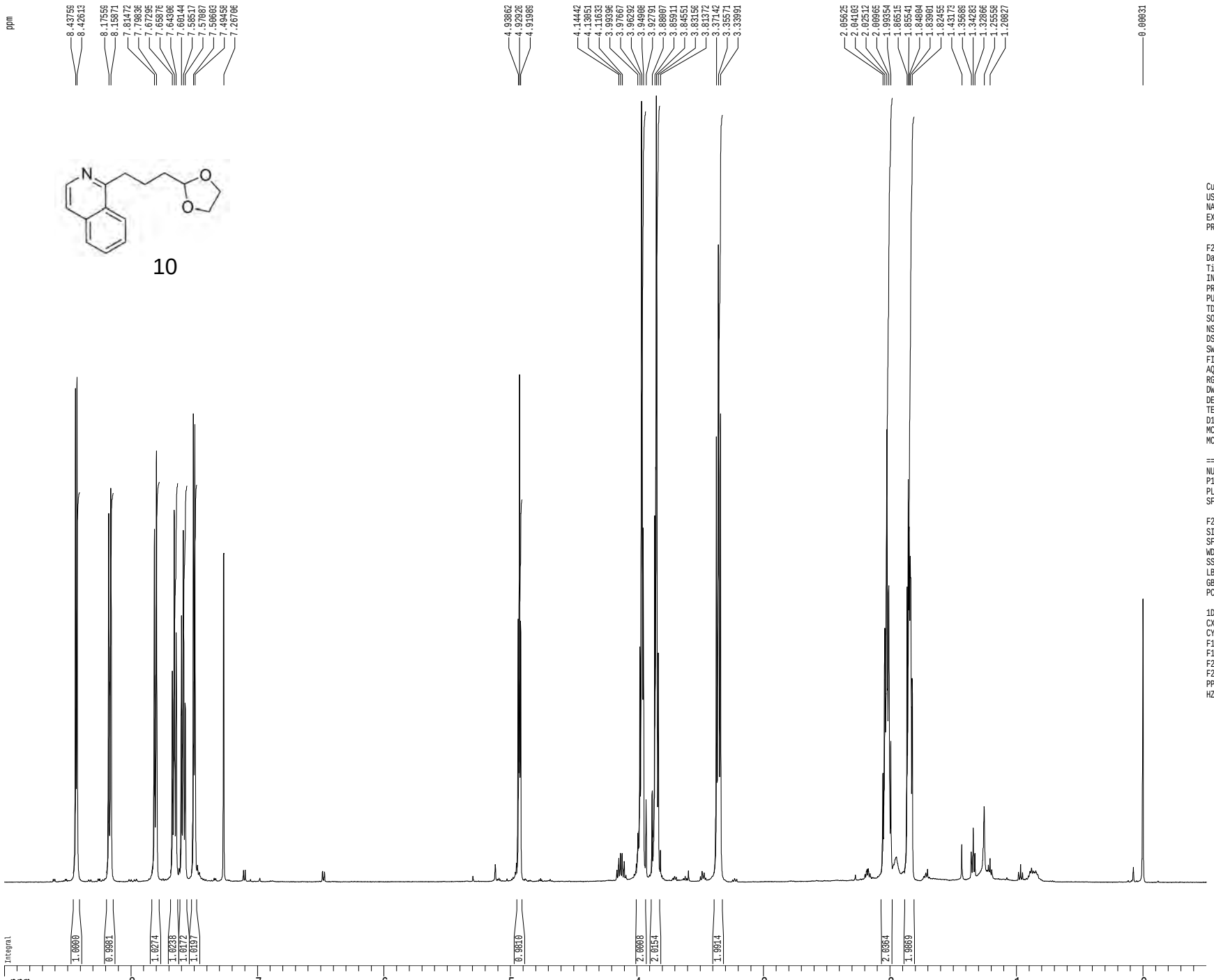
======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.50 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1         SINE.100
GPNAM2         SINE.100
GPX1               0.00 %
GPX2               0.00 %
GPY1               0.00 %
GPY2               0.00 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7804094 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 2.00

1D NMR plot parameters
CX                22.80 cm
CY                15.65 cm
F1P             220.000 ppm
F1            27671.69 Hz
F2P              -5.000 ppm
F2             -628.90 Hz
PPMCM          9.86842 ppm/cm
HZCM         1241.25415 Hz/cm
```

1H spectrum



Current Data Parameters
USER mharri
NAME MRH-VII-241-1HNMR
EXPNO 1
PROCNO 1

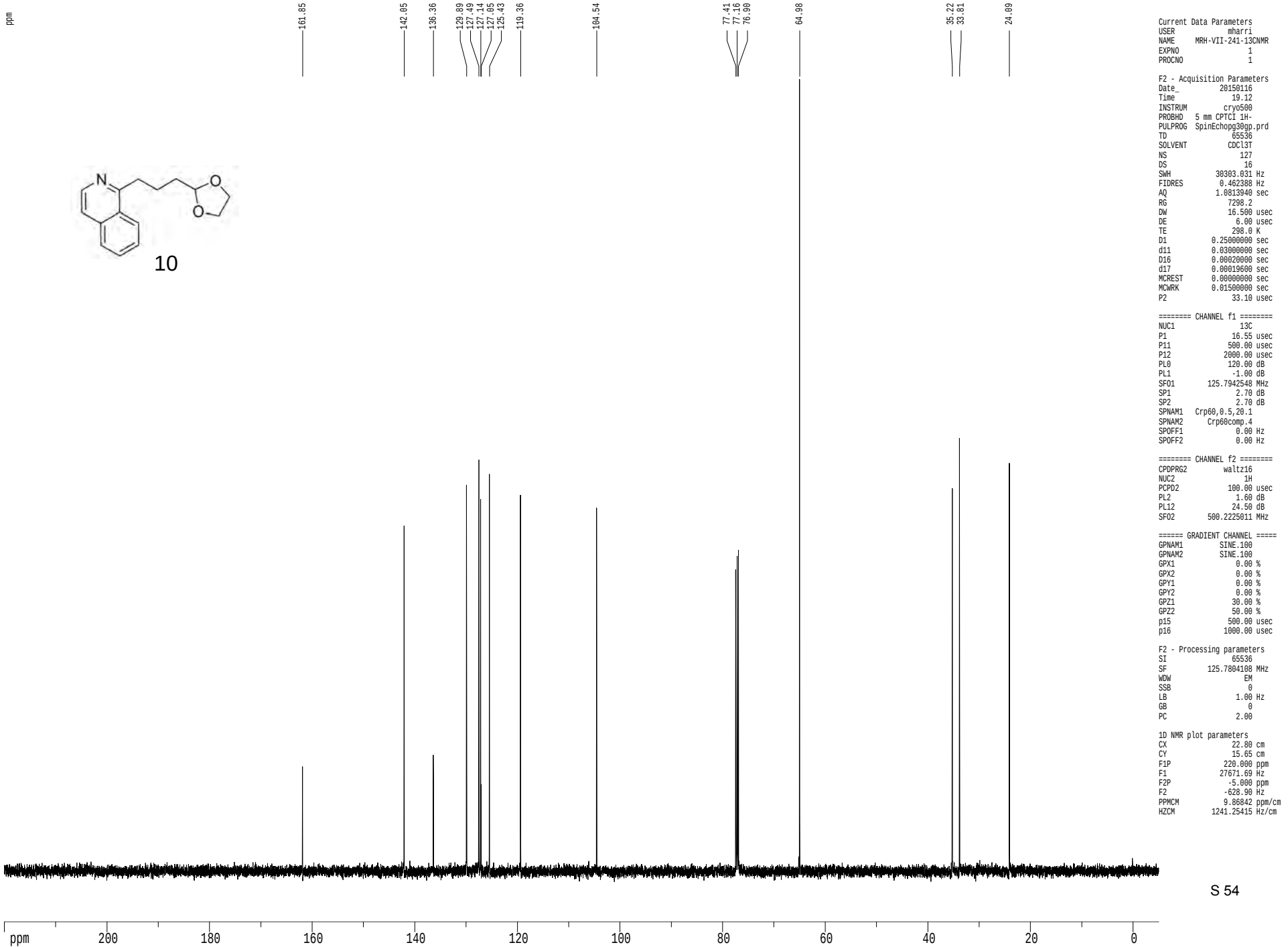
F2 - Acquisition Parameters
Date_ 20150116
Time 19.09
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG zg30
TD 81728
SOLVENT CDCl3
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 5.0998774 sec
RG 5.7
DW 62.400 usec
DE 6.00 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======== CHANNEL f1 ========
NUC1 1H
P1 7.50 usec
PL1 1.60 dB
SFO1 500.2235015 MHz

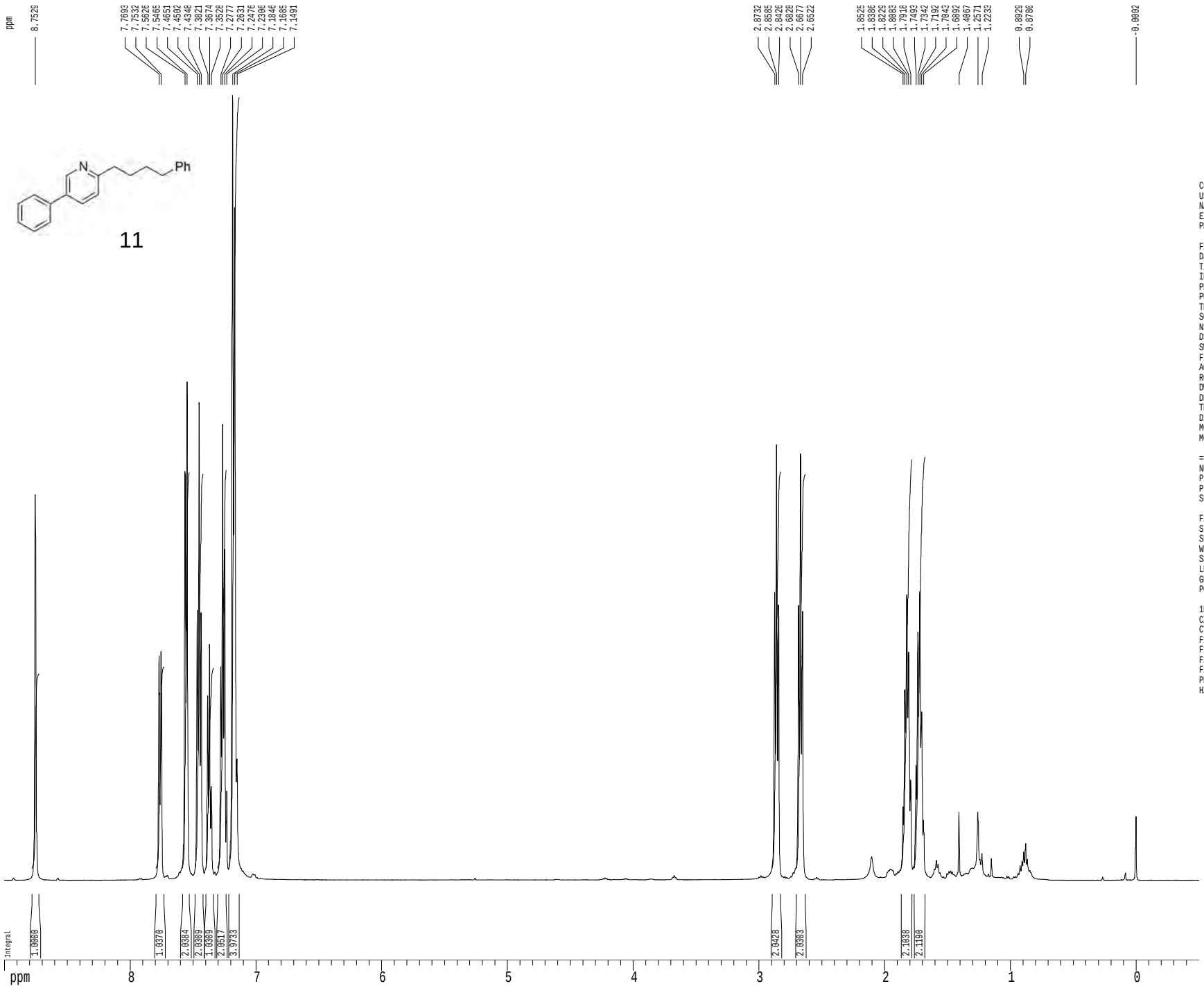
F2 - Processing parameters
SI 65536
SF 500.2200280 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 4.00

1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 9.000 ppm
F1 4501.98 Hz
F2P -0.500 ppm
F2 -250.11 Hz
PPMCM 0.41667 ppm/cm
HZCM 208.42502 Hz/cm

Z-restored spin-echo 13C spectrum with 1H decoupling



1H spectrum



Current Data Parameters
USER mharri
NAME MRH-VII-261-1HNMR
EXPNO 1
PROCNO 1

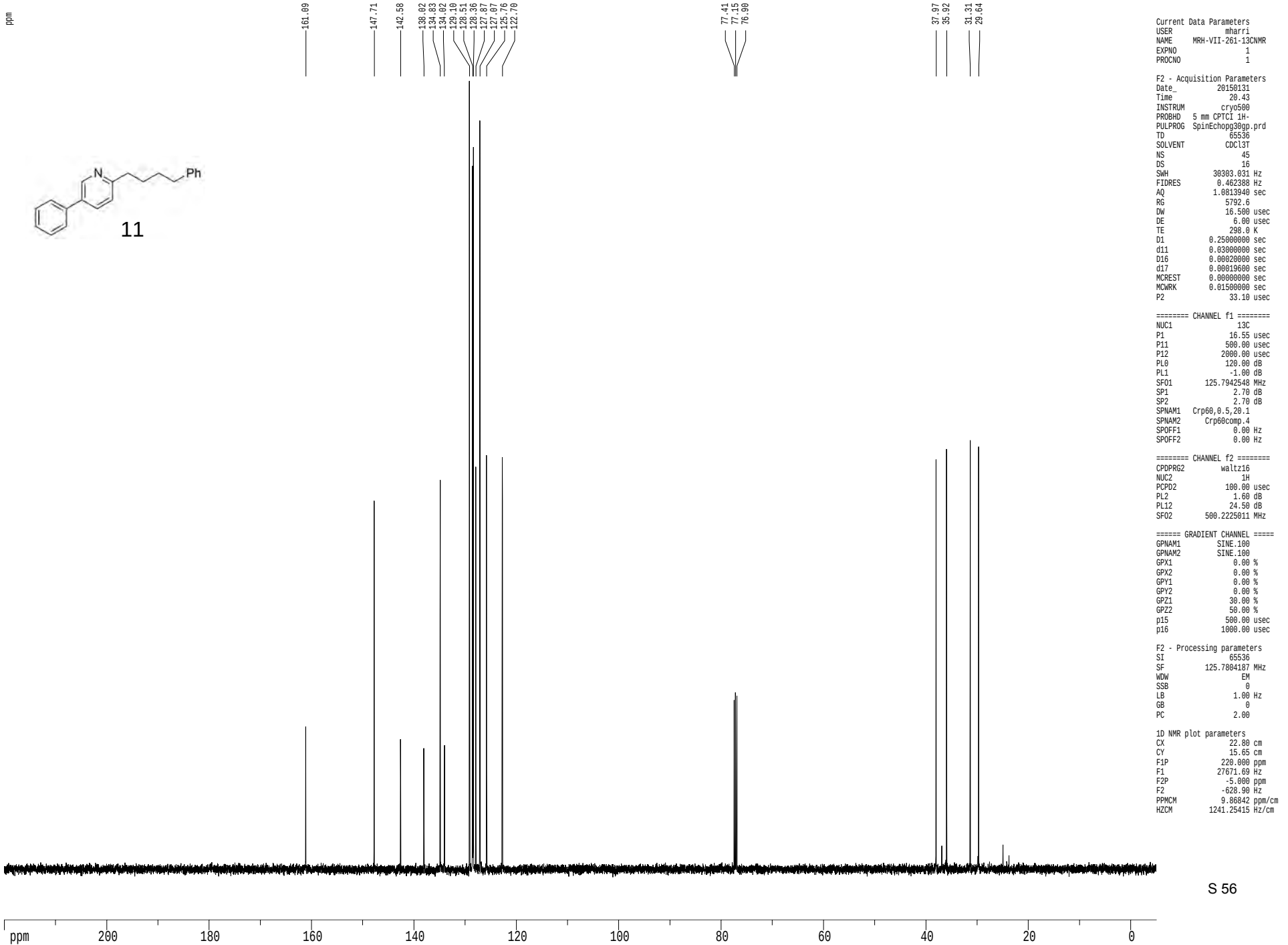
F2 - Acquisition Parameters
Date_ 20150131
Time 20.40
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG zg30
TD 81728
SOLVENT CDCl3T
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 5.0998774 sec
RG 4
DW 62.400 usec
DE 6.00 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======== CHANNEL f1 ========
NUC1 1H
P1 7.50 usec
PL1 1.60 dB
SFO1 500.2235015 MHz

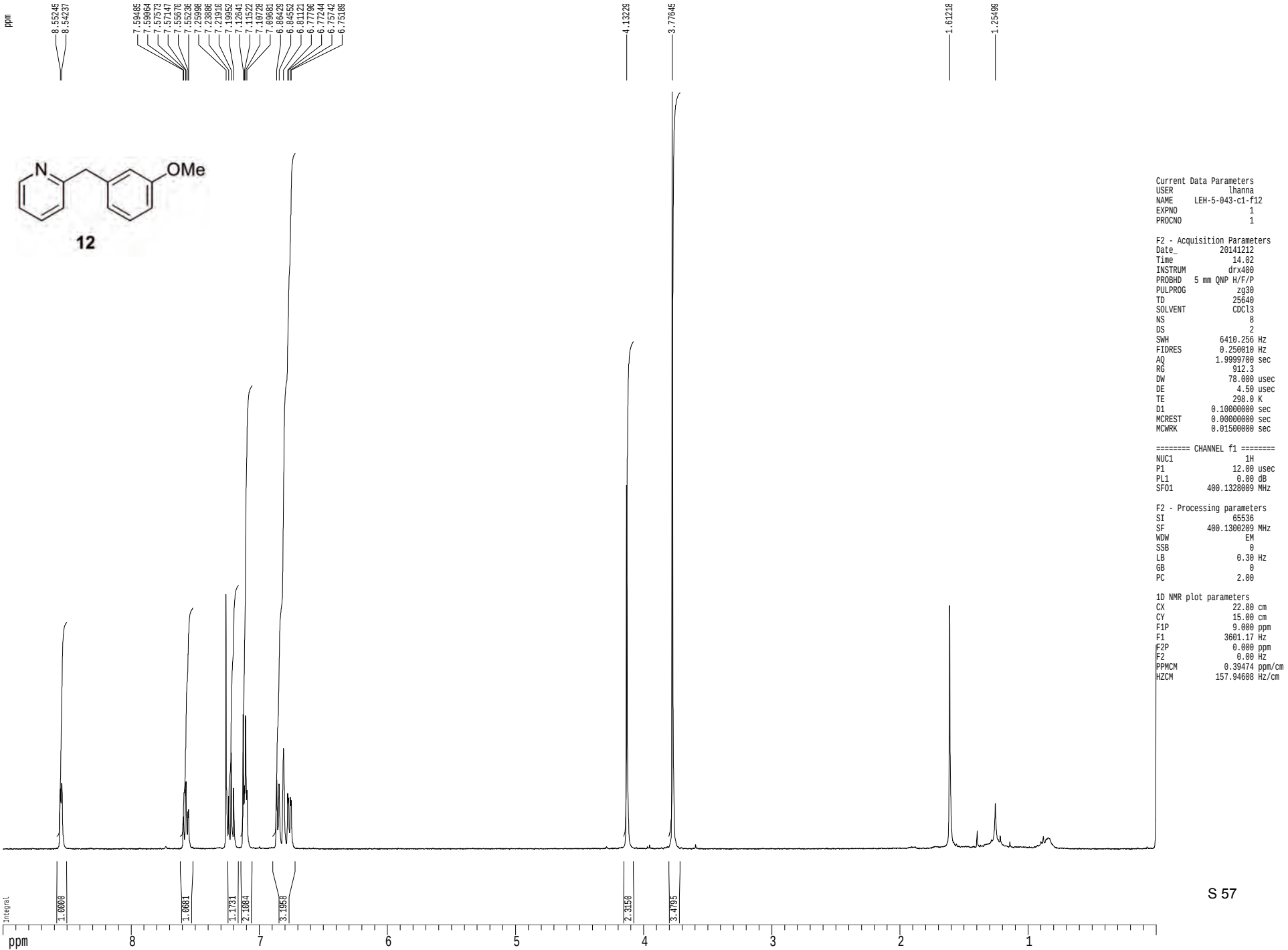
F2 - Processing parameters
SI 65536
SF 500.2200454 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 4.00

1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 9.000 ppm
F1 4501.98 Hz
F2P -0.500 ppm
F2 -250.11 Hz
PPMCM 0.41667 ppm/cm
HZCM 208.42502 Hz/cm

Z-restored spin-echo 13C spectrum with 1H decoupling



1H spectrum



Current Data Parameters
USER lhanna
NAME LEH-5-043-c1-f12
EXPNO 1
PROCNO 1

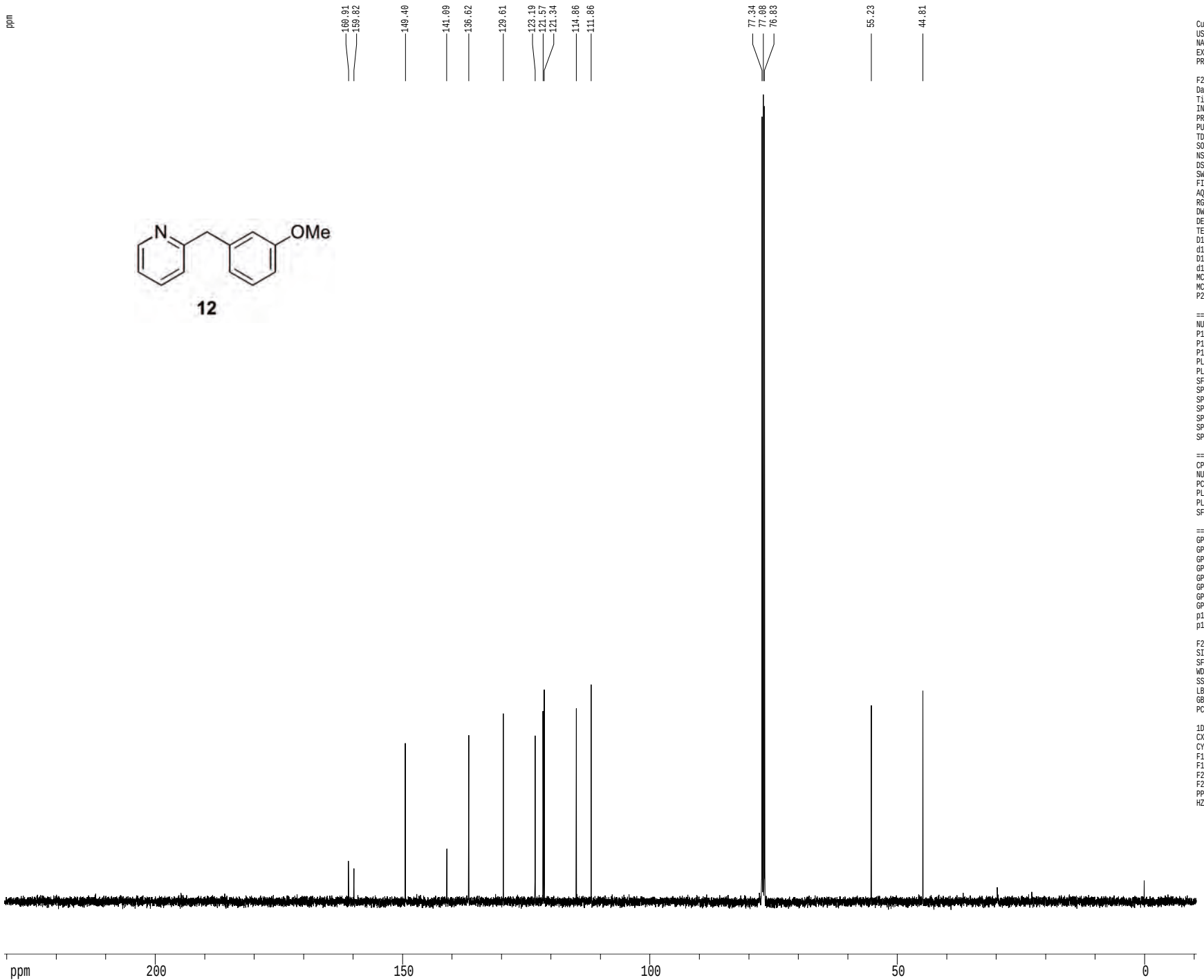
F2 - Acquisition Parameters
Date_ 20141212
Time 14.02
INSTRUM drx400
PROBHD 5 mm QNP H/F/P
PULPROG zg30
TD 25640
SOLVENT CDCl3
NS 8
DS 2
SWH 6410.256 Hz
FIDRES 0.250010 Hz
AQ 1.9999700 sec
RG 912.3
DW 78.000 usec
DE 4.50 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 0.00 dB
SFO1 400.1328009 MHz

F2 - Processing parameters
SI 65536
SF 400.1300209 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 9.000 ppm
F1 3601.17 Hz
F2P 0.000 ppm
F2 0.00 Hz
PPMCM 0.39474 ppm/cm
HZCM 157.94608 Hz/cm

Z-restored spin-echo 13C spectrum with 1H decoupling




```
Current Data Parameters
USER                lhanna
NAME      LEH-5-043-c1-f12-C13
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_           20141212
Time                16.30
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                  65536
SOLVENT             CDCl3
NS                   1024
DS                     16
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ              1.0813940 sec
RG                 2896.3
DW                16.500 usec
DE                 6.00 usec
TE                 298.0 K
D1             0.25000000 sec
d11            0.03000000 sec
D16            0.00020000 sec
d17            0.00019600 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec
P2                33.10 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                2.70 dB
SP2                2.70 dB
SPNAM1   Crp60,0.5,20.1
SPNAM2      Crp60comp.4
SPOFF1               0.00 Hz
SPOFF2               0.00 Hz

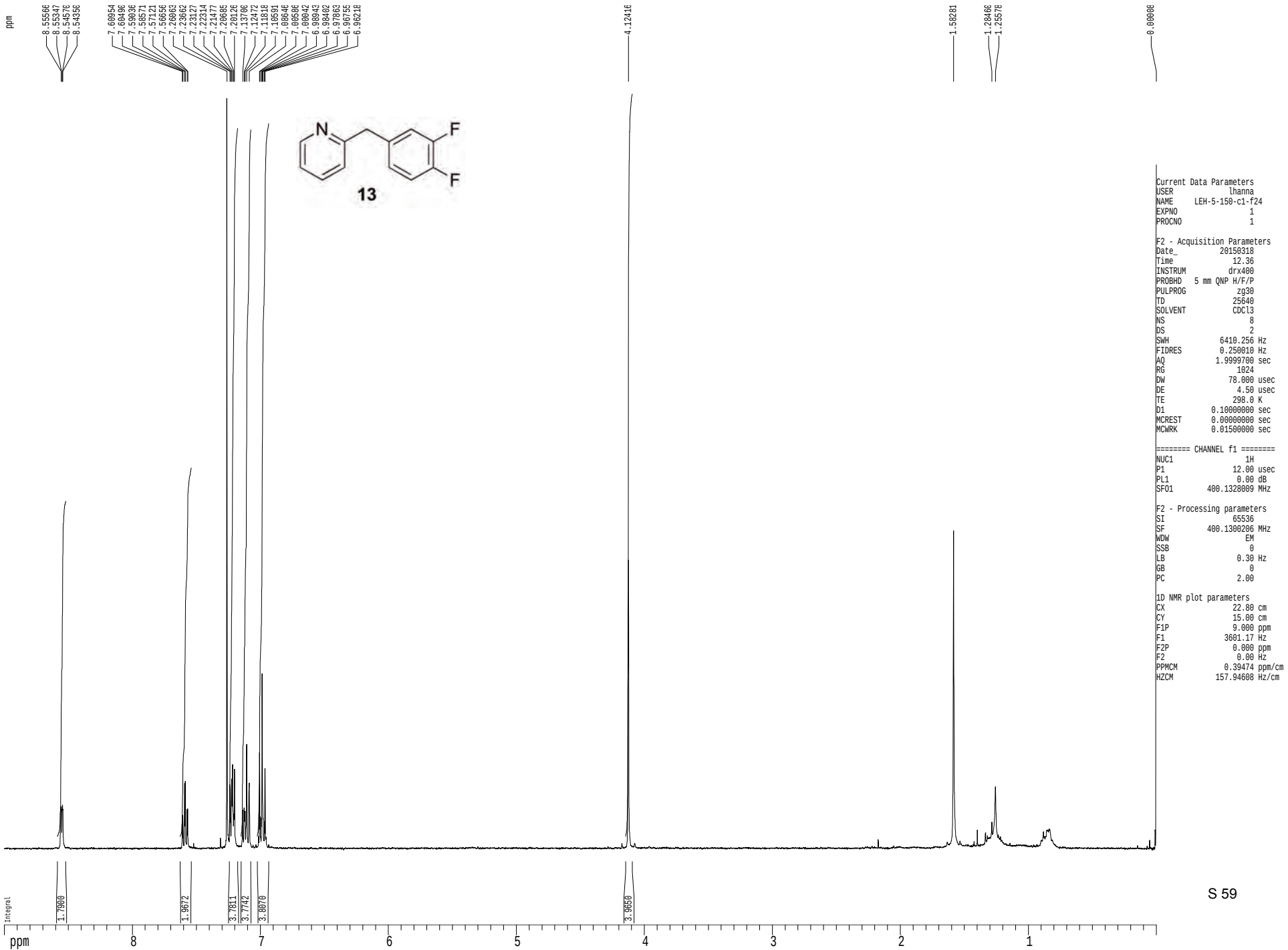
======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2             100.00 usec
PL2                1.60 dB
PL12              24.50 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1          SINE.100
GPNAM2          SINE.100
GPX1                0.00 %
GPX2                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                  65536
SF           125.7804190 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   2.00

1D NMR plot parameters
CX                  22.80 cm
CY                  15.65 cm
F1P              230.460 ppm
F1              28987.37 Hz
F2P              -10.460 ppm
F2              -1315.66 Hz
PPMCM           10.56667 ppm/cm
HZCM          1329.08032 Hz/cm
```

1H spectrum




```
Current Data Parameters
USER              lhanna
NAME      LEH-5-150-c1-f24
EXPNO                   1
PROCNO                  1

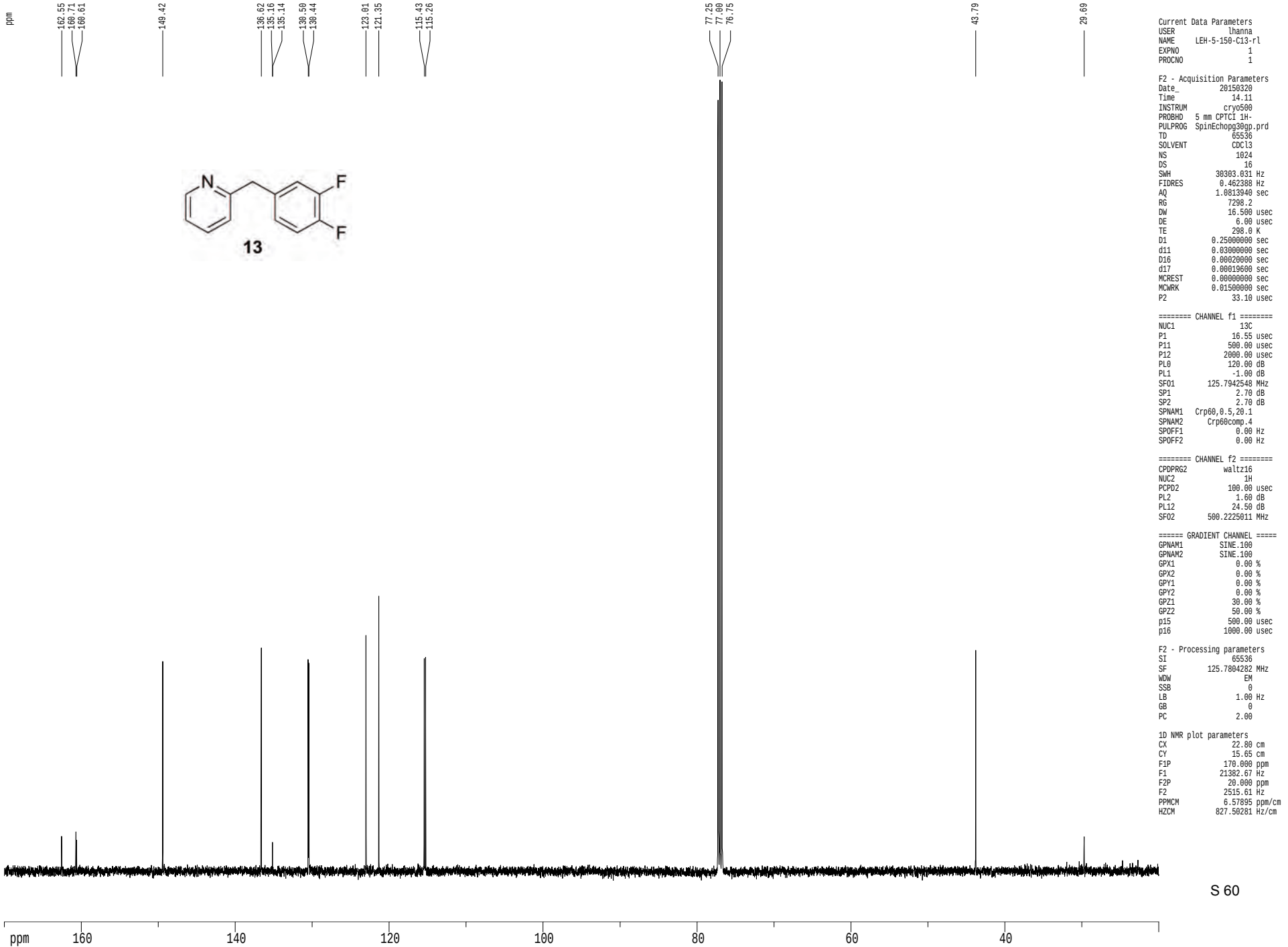
F2 - Acquisition Parameters
Date_            20150318
Time                12.36
INSTRUM           drx400
PROBHD   5 mm QNP H/F/P
PULPROG              zg30
TD                  25640
SOLVENT             CDCl3
NS                      8
DS                      2
SWH            6410.256 Hz
FIDRES         0.250010 Hz
AQ             1.9999700 sec
RG                   1024
DW                78.000 usec
DE                 4.50 usec
TE                298.0 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                 12.00 usec
PL1                 0.00 dB
SFO1         400.1328009 MHz

F2 - Processing parameters
SI                  65536
SF           400.1300206 MHz
WDW                    EM
SSB                     0
LB                 0.30 Hz
GB                      0
PC                 2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                9.000 ppm
F1              3601.17 Hz
F2P                0.000 ppm
F2                 0.00 Hz
PPMCM           0.39474 ppm/cm
HZCM          157.94608 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling




```
Current Data Parameters
USER                lhanna
NAME      LEH-5-150-C13-rl
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20150320
Time                 14.11
INSTRUM            cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                   65536
SOLVENT              CDCl3
NS                    1024
DS                      16
SWH              30303.031 Hz
FIDRES           0.462388 Hz
AQ               1.0813940 sec
RG                 7298.2
DW                 16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1              0.25000000 sec
d11             0.03000000 sec
D16             0.00020000 sec
d17             0.00019600 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec
P2                  33.10 usec

======== CHANNEL f1 ========
NUC1                  13C
P1                  16.55 usec
P11                500.00 usec
P12               2000.00 usec
PL0                120.00 dB
PL1                 -1.00 dB
SFO1          125.7942548 MHz
SP1                  2.70 dB
SP2                  2.70 dB
SPNAM1    Crp60,0.5,20.1
SPNAM2       Crp60comp.4
SPOFF1               0.00 Hz
SPOFF2               0.00 Hz

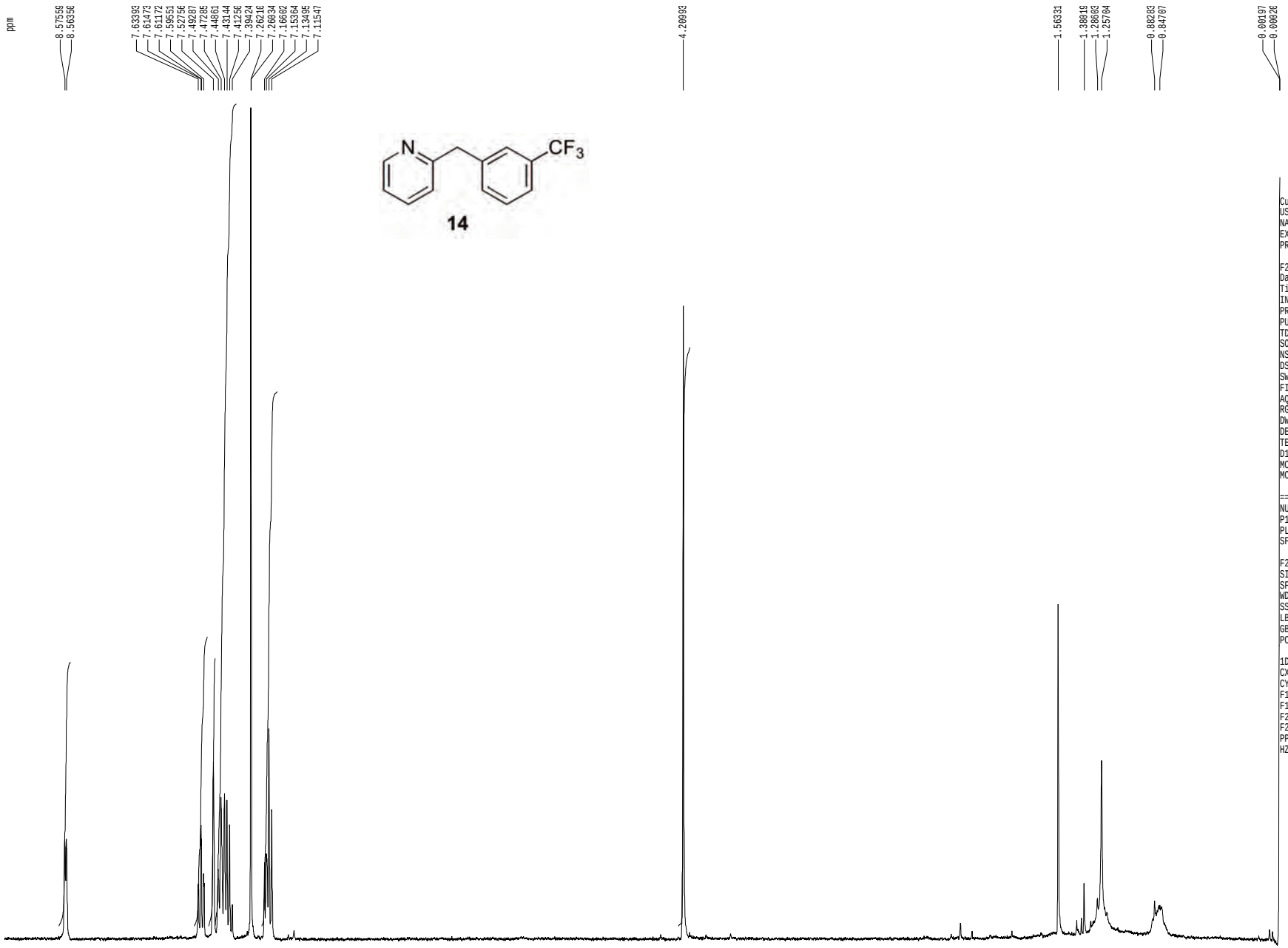
======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12                24.50 dB
SFO2          500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1           SINE.100
GPNAM2           SINE.100
GPX1                 0.00 %
GPX2                 0.00 %
GPY1                 0.00 %
GPY2                 0.00 %
GPZ1                30.00 %
GPZ2                50.00 %
p15                500.00 usec
p16               1000.00 usec

F2 - Processing parameters
SI                   65536
SF            125.7804282 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   2.00

1D NMR plot parameters
CX                  22.80 cm
CY                  15.65 cm
F1P               170.000 ppm
F1                21382.67 Hz
F2P                20.000 ppm
F2                 2515.61 Hz
PPMCM              6.57895 ppm/cm
HZCM             827.50281 Hz/cm
```

1H spectrum




```
Current Data Parameters
USER              lhanna
NAME      LEH-5-068-c2-f16
EXPNO                   1
PROCNO                  1

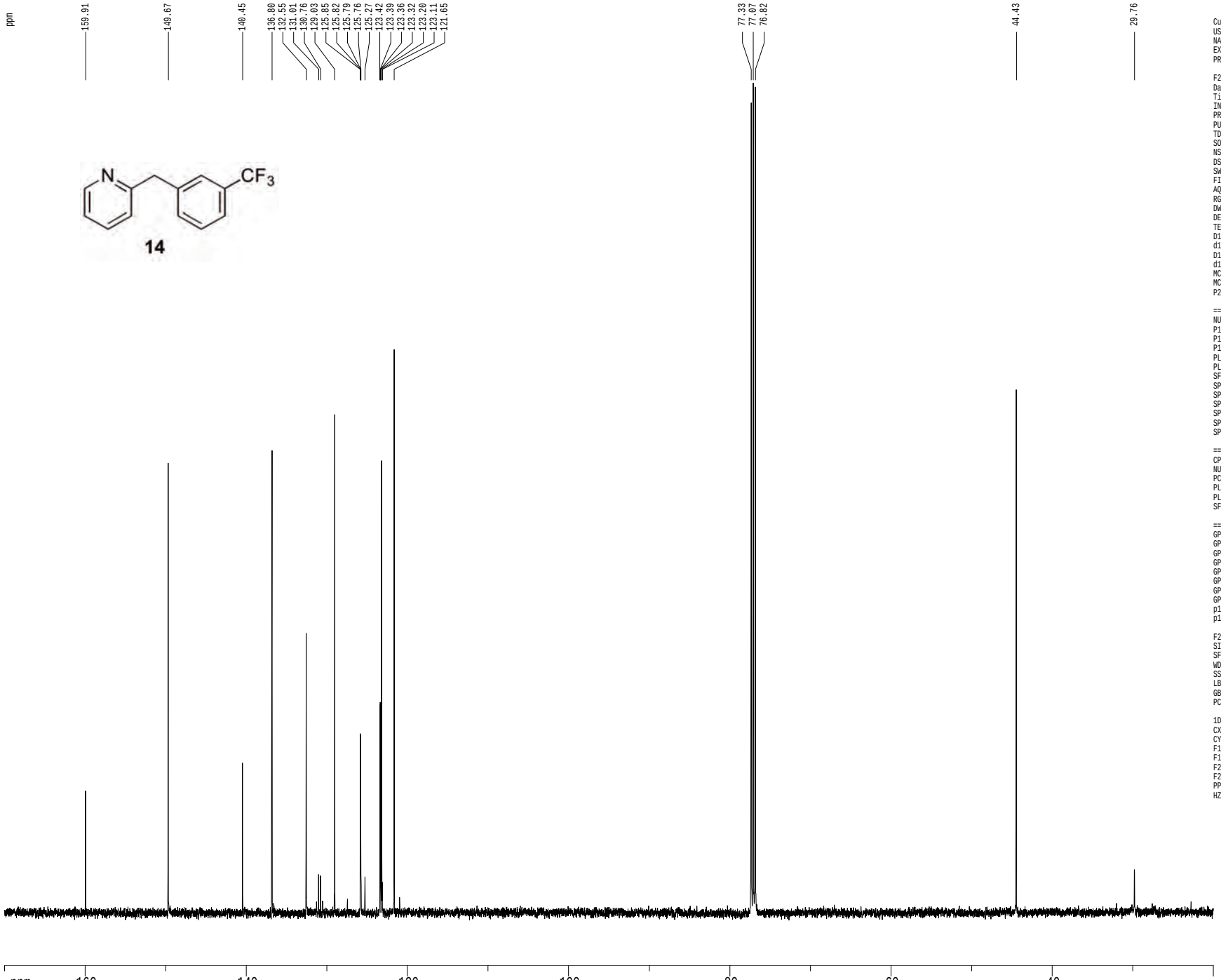
F2 - Acquisition Parameters
Date_            20150124
Time                17.48
INSTRUM           drx400
PROBHD   5 mm QNP H/F/P
PULPROG              zg30
TD                  25640
SOLVENT             CDCl3
NS                      8
DS                      2
SWH            6410.256 Hz
FIDRES         0.250010 Hz
AQ             1.9999700 sec
RG                 1149.4
DW                78.000 usec
DE                 4.50 usec
TE                298.0 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                 12.00 usec
PL1                 0.00 dB
SFO1         400.1328009 MHz

F2 - Processing parameters
SI                  65536
SF           400.1300199 MHz
WDW                    EM
SSB                     0
LB                 0.30 Hz
GB                      0
PC                 2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                9.000 ppm
F1               3601.17 Hz
F2P                0.000 ppm
F2                 0.00 Hz
PPMCM           0.39474 ppm/cm
HZCM          157.94606 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



Current Data Parameters
USER lhanna
NAME LEH-5-068-C2-C13-real
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20150129
Time 15.01
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG SpinEchopg30gp.prd
TD 65536
SOLVENT CDCl3
NS 1281
DS 16
SWH 30303.031 Hz
FIDRES 0.462398 Hz
AQ 1.0813940 sec
RG 5792.6
DW 16.500 usec
DE 6.00 usec
TE 298.0 K
D1 0.50000000 sec
d11 0.03000000 sec
D16 0.00020000 sec
d17 0.00019600 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
P2 33.10 usec

======== CHANNEL f1 ========
NUC1 13C
P1 16.55 usec
P11 500.00 usec
P12 2000.00 usec
PL0 120.00 dB
PL1 -1.00 dB
SFO1 125.7942548 MHz
SP1 2.70 dB
SP2 2.70 dB
SPNAM1 Crp60,0.5,20.1
SPNAM2 Crp60comp.4
SPOFF1 0.00 Hz
SPOFF2 0.00 Hz

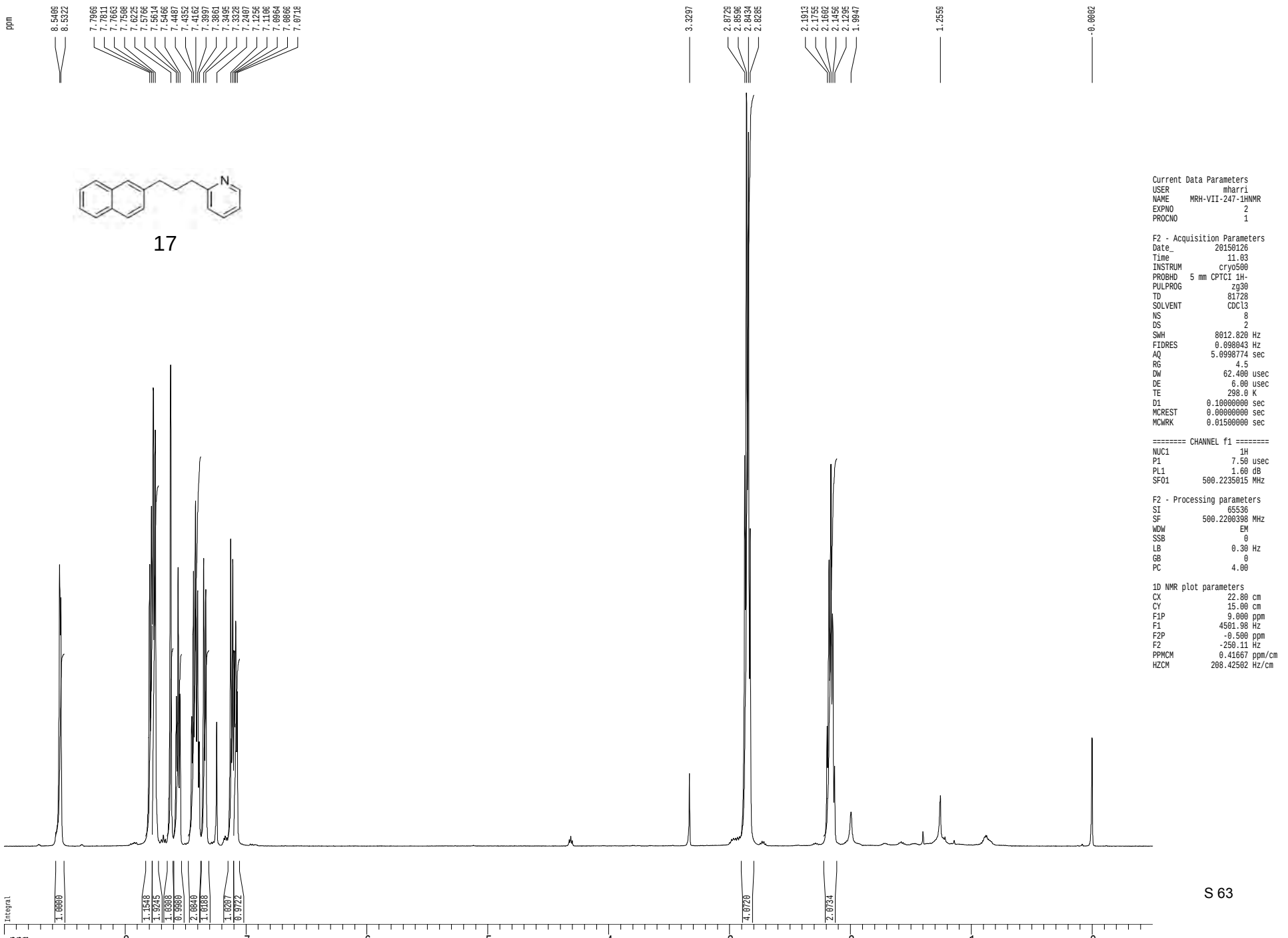
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 1.60 dB
PL12 24.50 dB
SFO2 500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1 SINE.100
GPNAM2 SINE.100
GPX1 0.00 %
GPX2 0.00 %
GPY1 0.00 %
GPY2 0.00 %
GPZ1 30.00 %
GPZ2 50.00 %
p15 500.00 usec
p16 1000.00 usec

F2 - Processing parameters
SI 65536
SF 125.7804190 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.80 cm
CY 15.65 cm
F1P 170.000 ppm
F1 21382.67 Hz
F2P 20.000 ppm
F2 2515.61 Hz
PPMCM 6.57895 ppm/cm
HZCM 827.50281 Hz/cm

1H spectrum



Current Data Parameters
USER mharri
NAME MRH-VII-247-1HNMR
EXPNO 2
PROCNO 1

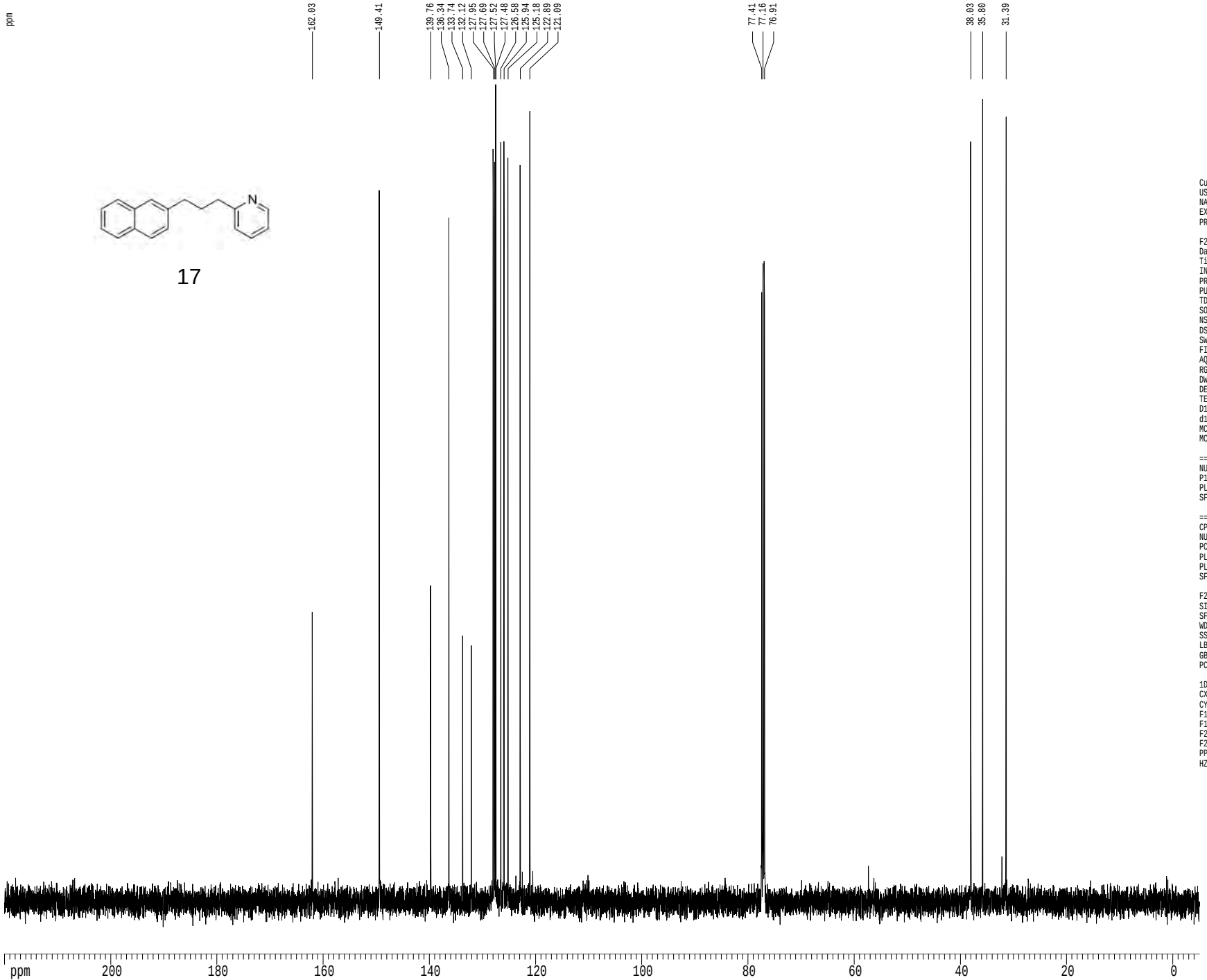
F2 - Acquisition Parameters
Date_ 20150126
Time 11.03
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG zg30
TD 81728
SOLVENT CDCl3
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 5.0998774 sec
RG 4.5
DW 62.400 usec
DE 6.00 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======== CHANNEL f1 ========
NUC1 1H
P1 7.50 usec
PL1 1.60 dB
SFO1 500.2235015 MHz

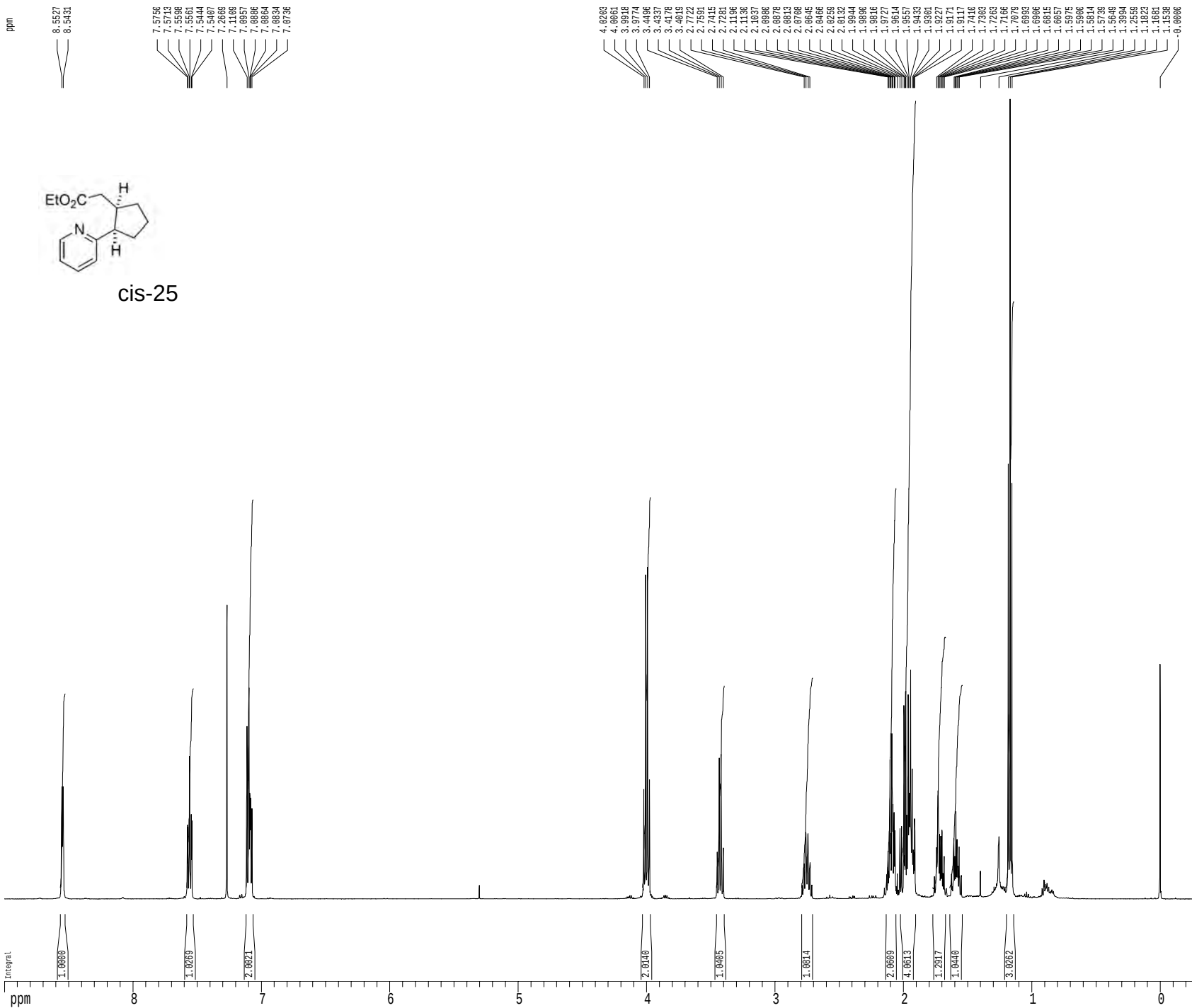
F2 - Processing parameters
SI 65536
SF 500.2200398 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 4.00

1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 9.000 ppm
F1 4501.98 Hz
F2P -0.500 ppm
F2 -250.11 Hz
PPMCM 0.41667 ppm/cm
HZCM 208.42502 Hz/cm

13C spectrum with 1H decoupling

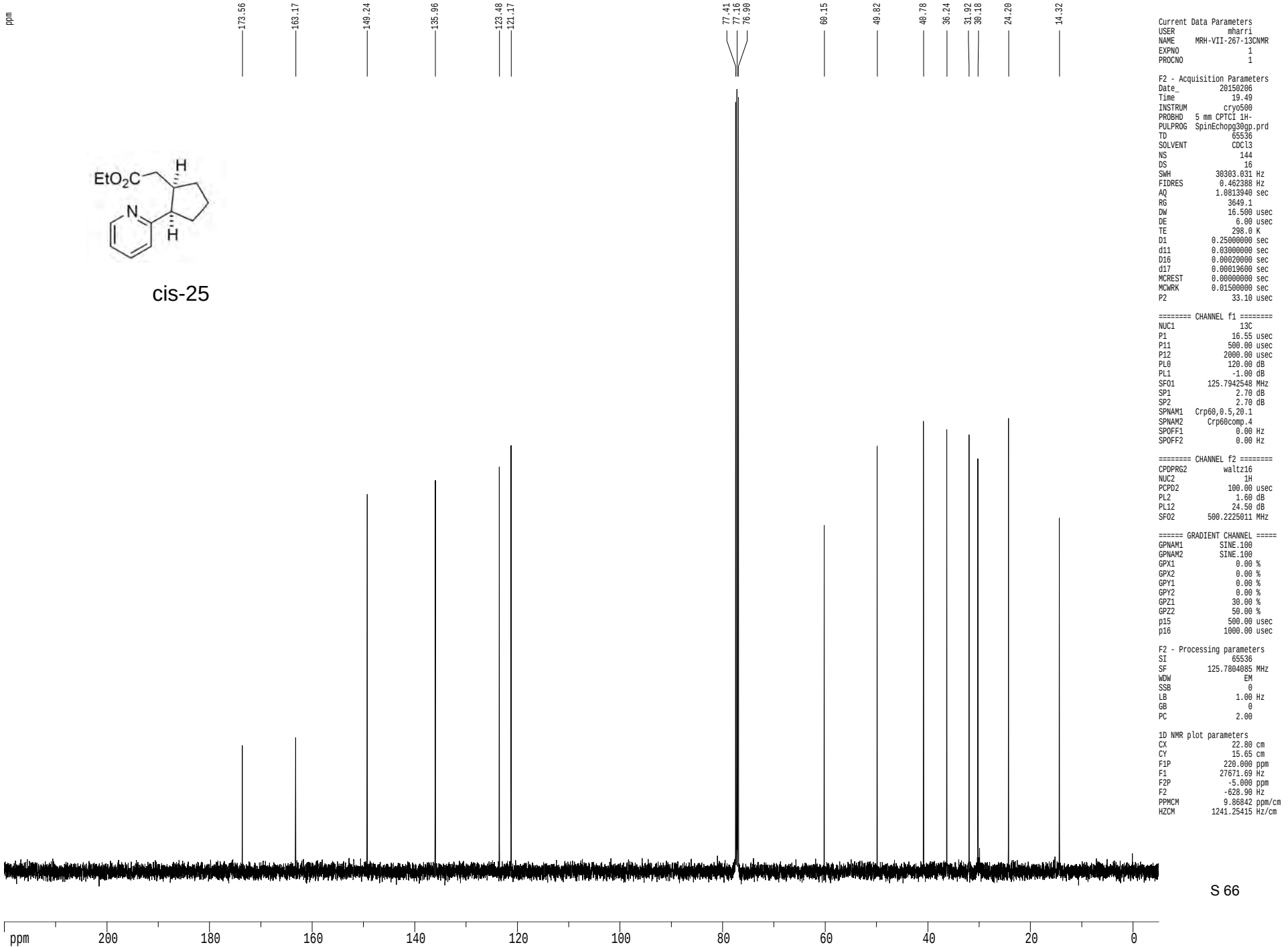


1H spectrum



cis-25

Z-restored spin-echo 13C spectrum with 1H decoupling




```
Current Data Parameters
USER              mharri
NAME      MRH-VII-267-13CNMR
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_           20150206
Time              19.49
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                   144
DS                    16
SWH            30303.031 Hz
FIDRES         0.462388 Hz
AQ             1.0813940 sec
RG                3649.1
DW                16.500 usec
DE                 6.00 usec
TE                298.0 K
D1             0.25000000 sec
d11            0.03000000 sec
D16            0.00020000 sec
d17            0.00019600 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec
P2                33.10 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                16.55 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1         125.7942548 MHz
SP1               2.70 dB
SP2               2.70 dB
SPNAM1   Crp60,0.5,20.1
SPNAM2      Crp60comp.4
SPOFF1               0.00 Hz
SPOFF2               0.00 Hz

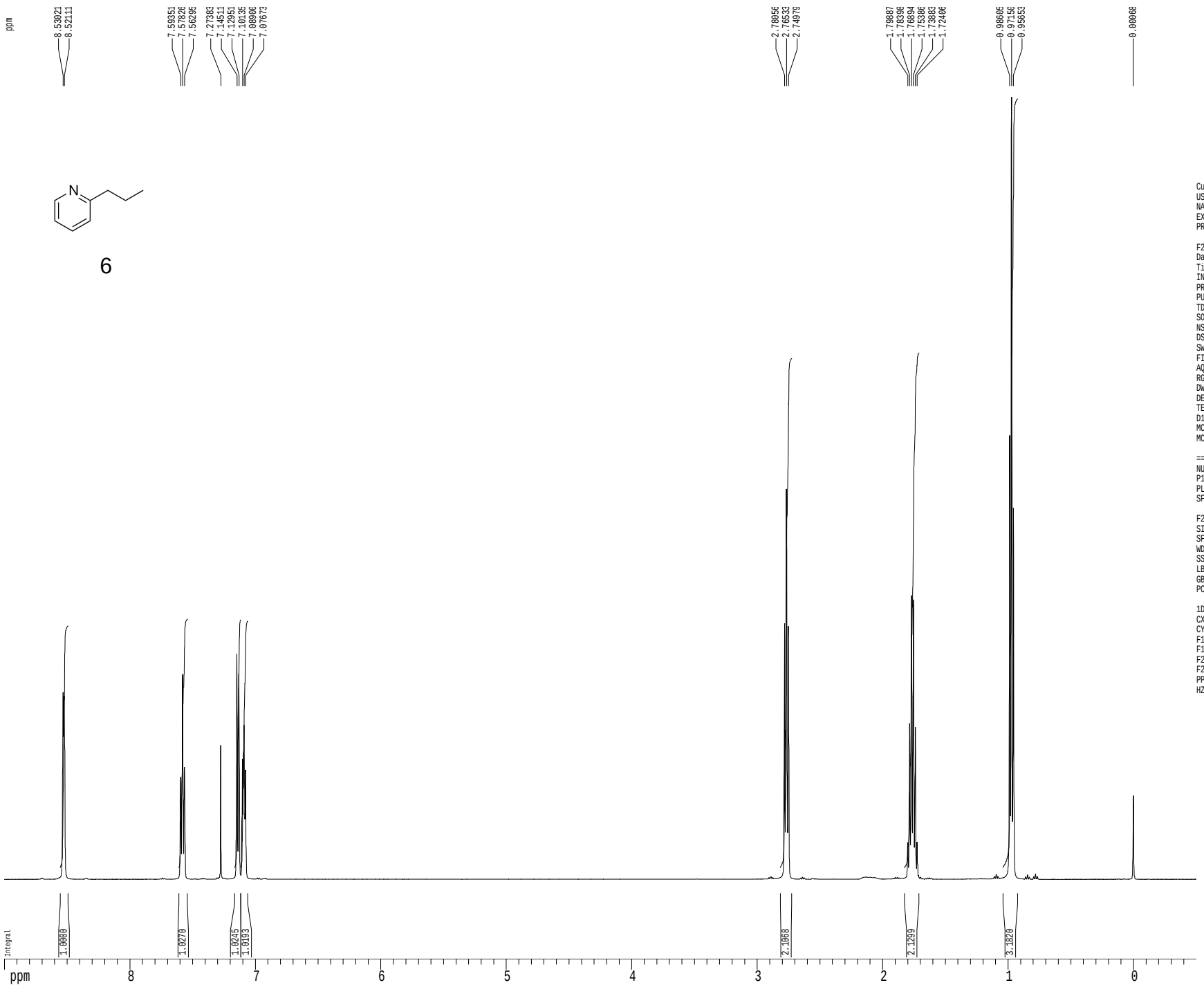
======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.50 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1          SINE.100
GPNAM2          SINE.100
GPX1                0.00 %
GPX2                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPZ1               30.00 %
GPZ2               50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7804085 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 2.00

1D NMR plot parameters
CX                22.80 cm
CY                15.65 cm
F1P             220.000 ppm
F1             27671.69 Hz
F2P              -5.000 ppm
F2              -628.90 Hz
PPMCM           9.86842 ppm/cm
HZCM         1241.25415 Hz/cm
```

1H spectrum




```
Current Data Parameters
USER                mharri
NAME      MRH-VII-283-1HNMR
EXPNO                    3
PROCNO                   1

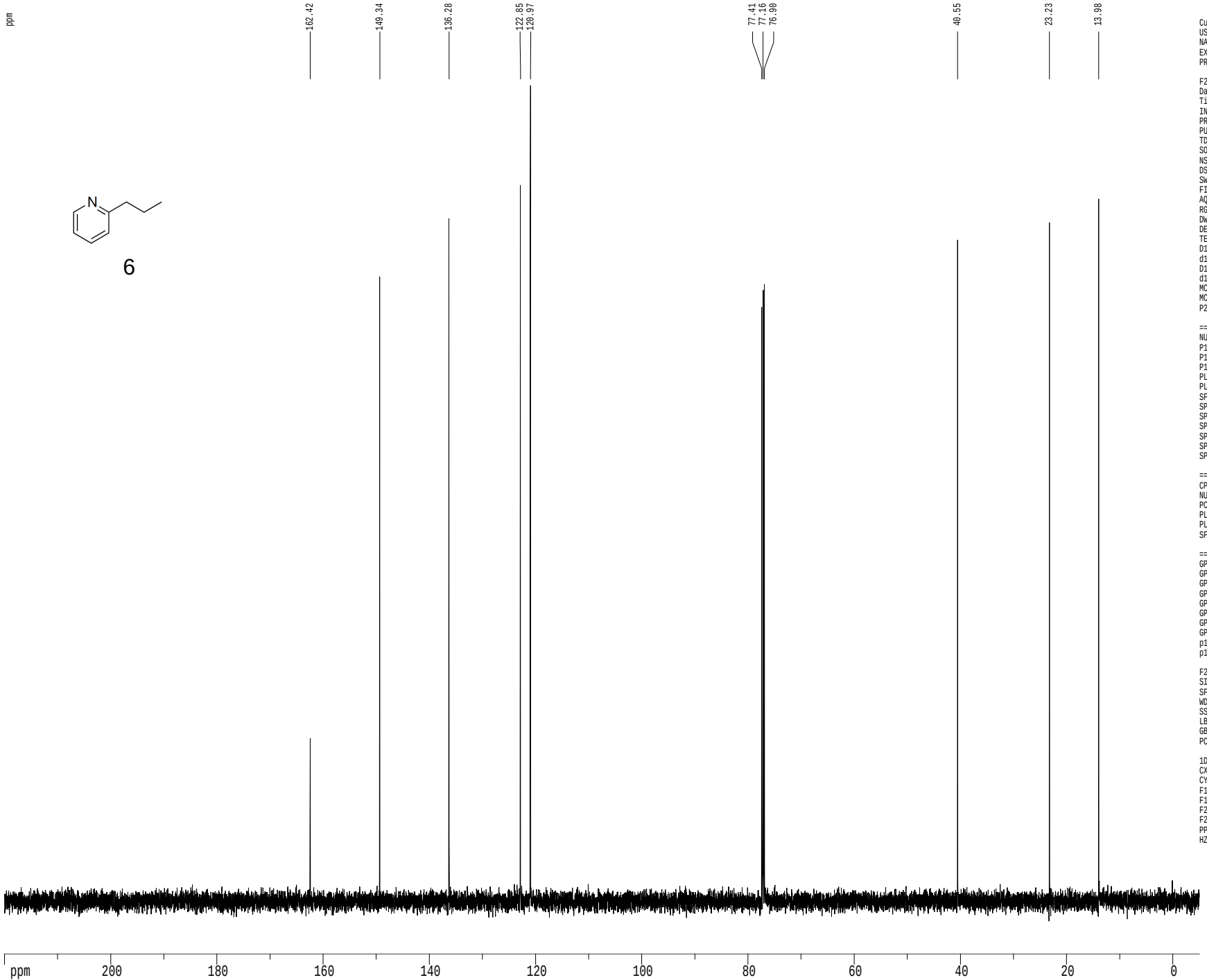
F2 - Acquisition Parameters
Date_            20150304
Time                17.30
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG              zg30
TD                  81728
SOLVENT             CDCl3
NS                      8
DS                      2
SWH              8012.820 Hz
FIDRES           0.098043 Hz
AQ               5.0998774 sec
RG                      8
DW                 62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1             0.10000000 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                    1H
P1                   7.50 usec
PL1                  1.60 dB
SFO1          500.2235015 MHz

F2 - Processing parameters
SI                   65536
SF            500.2200244 MHz
WDW                     EM
SSB                      0
LB                  0.30 Hz
GB                       0
PC                   4.00

1D NMR plot parameters
CX                  22.80 cm
CY                  15.00 cm
F1P                 9.000 ppm
F1                4501.98 Hz
F2P                -0.500 ppm
F2                 -250.11 Hz
PPMCM            0.41667 ppm/cm
HZCM           208.42502 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling




```
Current Data Parameters
USER                mharri
NAME      MRH-VII-283-13CNMR
EXPNO                    3
PROCNO                   1

F2 - Acquisition Parameters
Date_            20150304
Time                17.33
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                  65536
SOLVENT             CDCl3
NS                     54
DS                     16
SWH             30303.031 Hz
FIDRES          0.462388 Hz
AQ              1.0813940 sec
RG                3649.1
DW                16.500 usec
DE                 6.00 usec
TE                298.0 K
D1             0.25000000 sec
d11            0.03000000 sec
D16            0.00020000 sec
d17            0.00019600 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec
P2                33.10 usec

======== CHANNEL f1 ========
NUC1                  13C
P1                 16.55 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                2.70 dB
SP2                2.70 dB
SPNAM1   Crp60,0.5,20.1
SPNAM2      Crp60comp.4
SPOFF1               0.00 Hz
SPOFF2               0.00 Hz

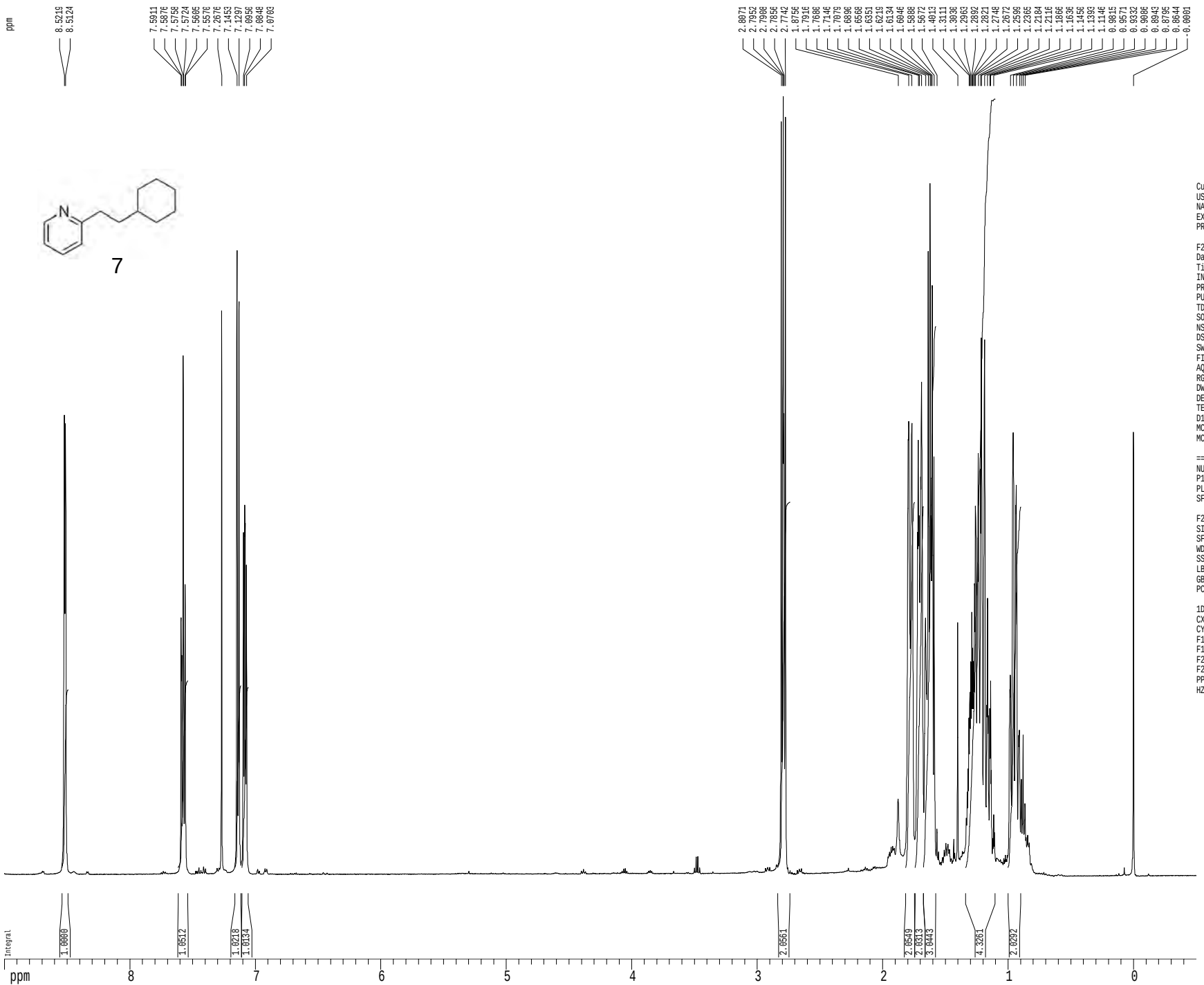
======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                1.60 dB
PL12              24.50 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1          SINE.100
GPNAM2          SINE.100
GPX1                0.00 %
GPX2                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

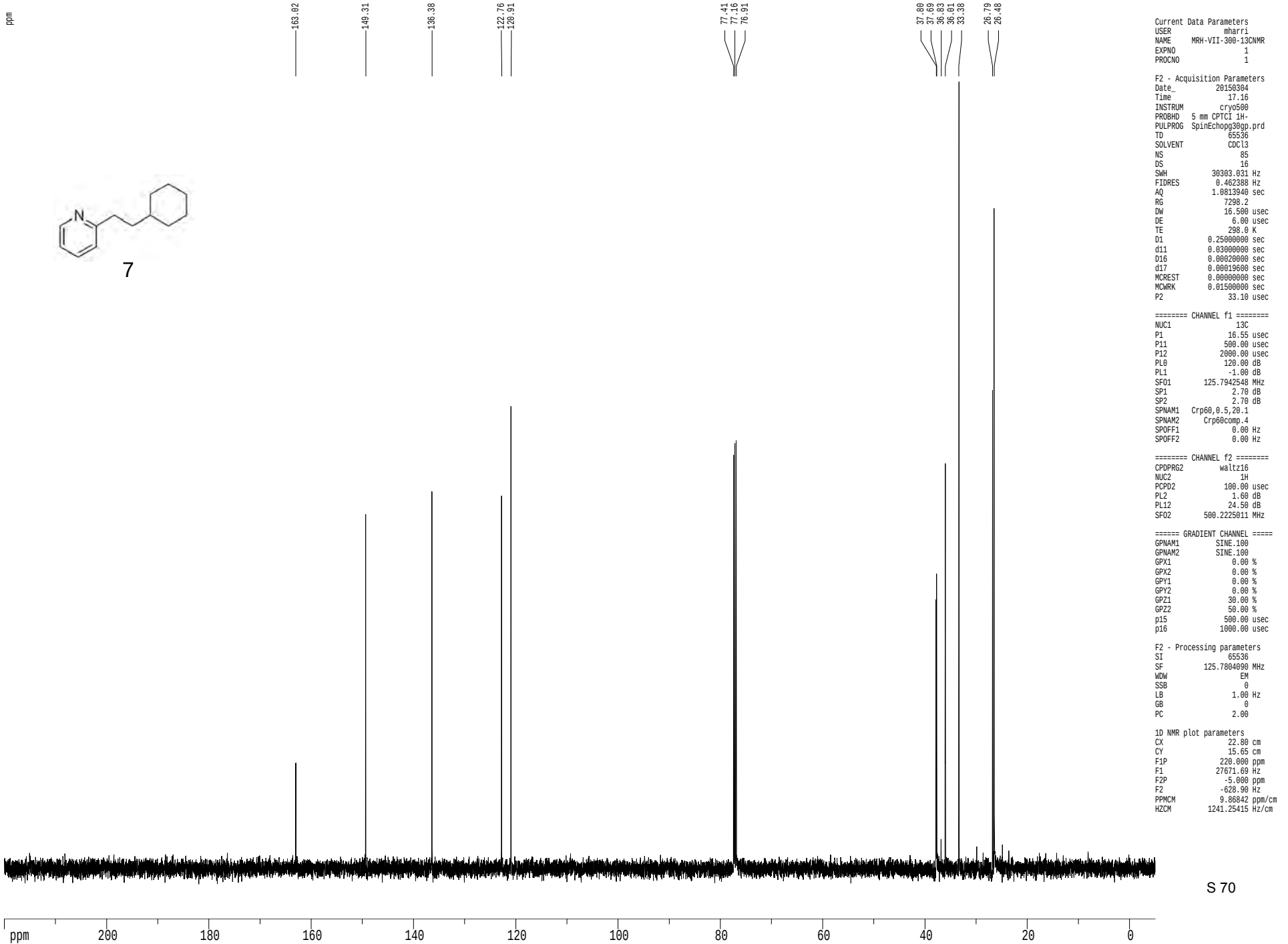
F2 - Processing parameters
SI                  65536
SF           125.7804099 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   2.00

1D NMR plot parameters
CX                  22.80 cm
CY                  15.65 cm
F1P               220.000 ppm
F1              27671.69 Hz
F2P                -5.000 ppm
F2               -628.90 Hz
PPMCM             9.86842 ppm/cm
HZCM          1241.25415 Hz/cm
```

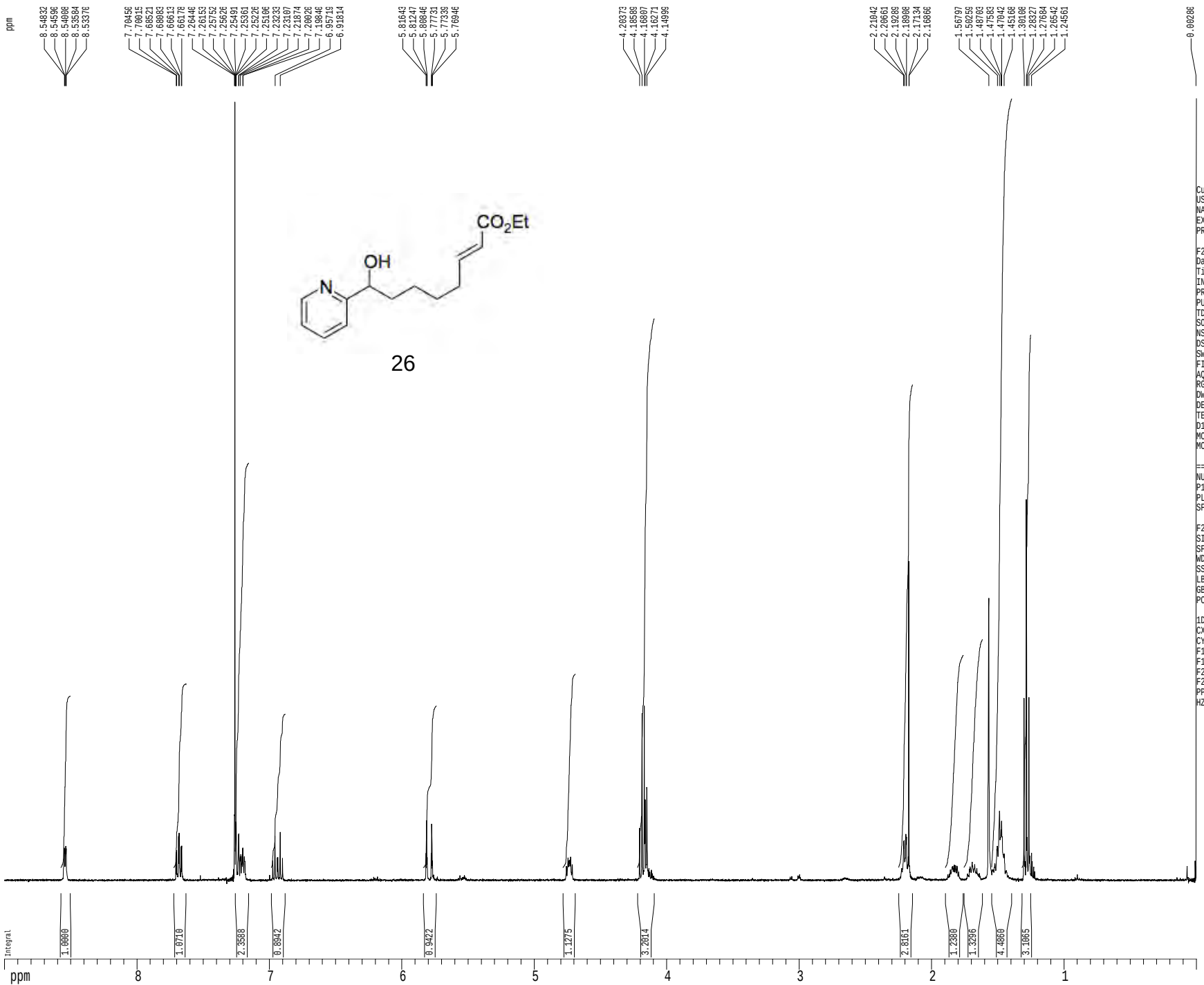
1H spectrum


ppm
8.5219
8.5124
7.5911
7.5876
7.5758
7.5724
7.5605
7.5578
7.2676
7.1453
7.1297
7.0956
7.0848
7.0703
2.8071
2.7952
2.7908
2.7856
2.7742
1.8756
1.7916
1.7688
1.7146
1.7073
1.6898
1.6568
1.6351
1.6219
1.6134
1.6046
1.5808
1.5672
1.4013
1.3111
1.3038
1.2963
1.2892
1.2821
1.2748
1.2672
1.2598
1.2385
1.2184
1.2116
1.1866
1.1636
1.1456
1.1393
1.1146
0.9815
0.9571
0.9332
0.9086
0.8943
0.8795
0.8644
-0.0001
N
7
Current Data Parameters
USER mharri
NAME MRH-VII-300-1HNMR
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20150304
Time 17.13
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG zg30
TD 81728
SOLVENT CDCl3
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 5.0998774 sec
RG 5.7
DW 62.400 usec
DE 6.00 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 7.50 usec
PL1 1.60 dB
SFO1 500.2235015 MHz
F2 - Processing parameters
SI 65536
SF 500.2200275 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 4.00
1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 9.000 ppm
F1 4501.98 Hz
F2P -0.500 ppm
F2 -250.11 Hz
PPMCM 0.41667 ppm/cm
HZCM 208.42502 Hz/cm
Integral
1.0000
1.0512
1.0218
1.0134
2.0561
2.0549
2.0313
3.0443
4.3261
2.0292
ppm
8
7
6
5
4
3
2
1
0

Z-restored spin-echo 13C spectrum with 1H decoupling



1H spectrum




```
Current Data Parameters
USER              lhanna
NAME          KD-1-083cl
EXPNO                 1
PROCNO                1

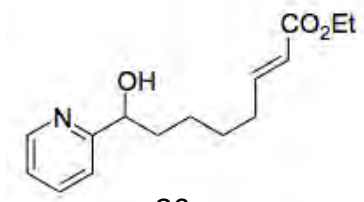
F2 - Acquisition Parameters
Date_          20161019
Time              15.33
INSTRUM          drx400
PROBHD   5 mm QNP H/F/P
PULPROG             zg30
TD                 25640
SOLVENT            CDCl3
NS                     8
DS                     2
SWH            6410.256 Hz
FIDRES         0.250010 Hz
AQ             1.9999700 sec
RG                 812.7
DW                78.000 usec
DE                 4.50 usec
TE                297.9 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                12.00 usec
PL1                0.00 dB
SFO1         400.1328009 MHz

F2 - Processing parameters
SI                 65536
SF           400.1300210 MHz
WDW                   no
SSB                    0
LB                 0.00 Hz
GB                     0
PC                 2.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P               9.000 ppm
F1              3601.17 Hz
F2P               0.000 ppm
F2                0.00 Hz
PPMCM          0.39474 ppm/cm
HZCM          157.94608 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



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Current Data Parameters
USER lhanna
NAME KD-1-083-6MEM-C13
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20161220
Time 13.34
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG SpinEchopg30gp.prd
TD 65536
SOLVENT CDCl3
NS 115
DS 16
SWH 30303.031 Hz
FIDRES 0.462388 Hz
AQ 1.0813940 sec
RG 7298.2
DW 16.500 usec
DE 6.00 usec
TE 298.0 K
D1 0.25000000 sec
d11 0.03000000 sec
D16 0.00020000 sec
d17 0.00019600 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
P2 33.10 usec

======== CHANNEL f1 ========
NUC1 13C
P1 16.55 usec
P11 500.00 usec
P12 2000.00 usec
PL0 120.00 dB
PL1 -1.00 dB
SFO1 125.7942548 MHz
SP1 2.70 dB
SP2 2.70 dB
SPNAM1 Crp60,0.5,20.1
SPNAM2 Crp60comp.4
SPOFF1 0.00 Hz
SPOFF2 0.00 Hz

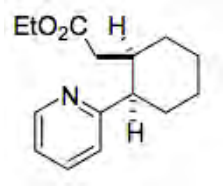
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 1.60 dB
PL12 24.50 dB
SFO2 500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1 SINE.100
GPNAM2 SINE.100
GPX1 0.00 %
GPX2 0.00 %
GPY1 0.00 %
GPY2 0.00 %
GPZ1 30.00 %
GPZ2 50.00 %
p15 500.00 usec
p16 1000.00 usec

F2 - Processing parameters
SI 65536
SF 125.7804069 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 2.00

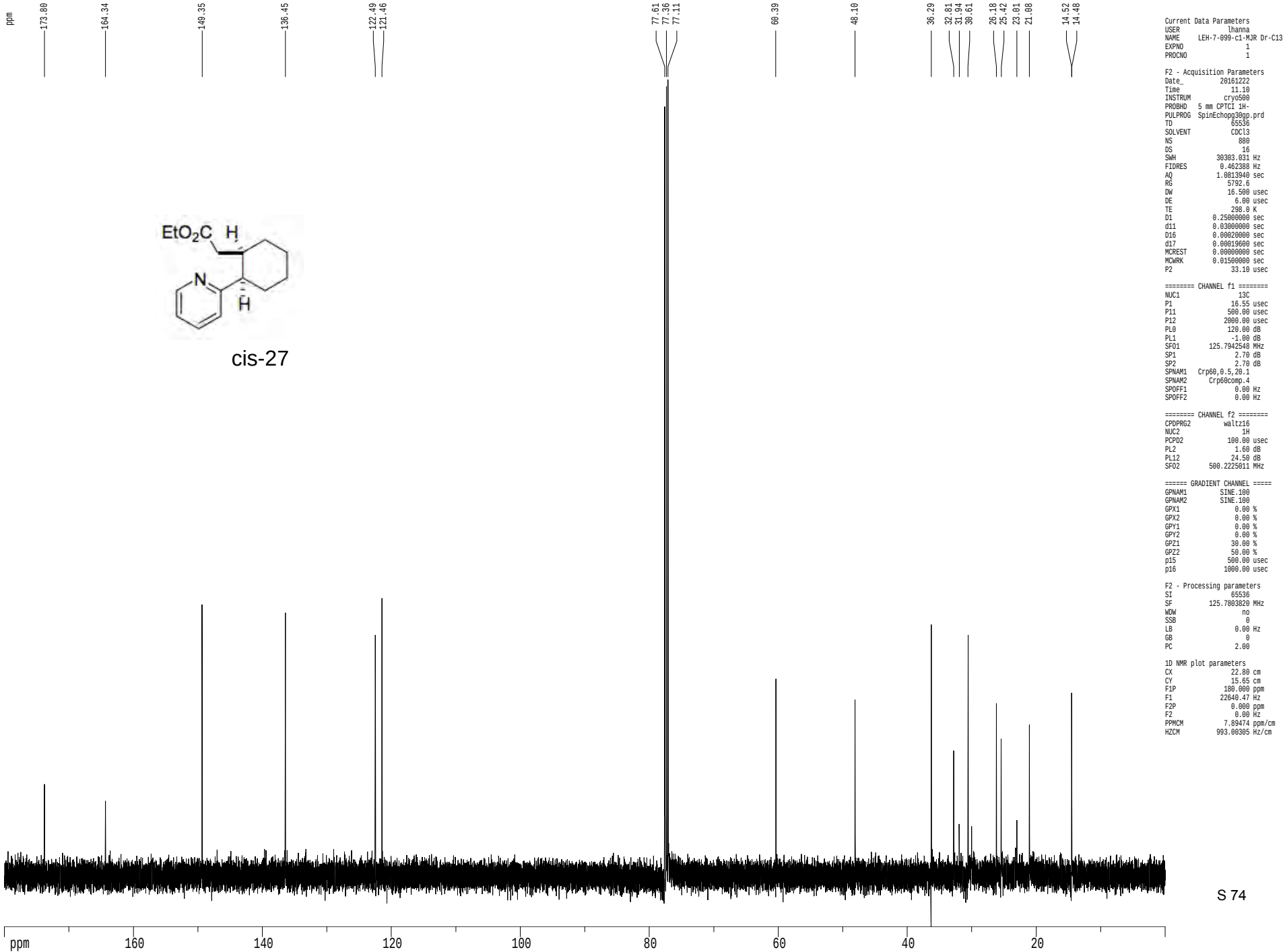
1D NMR plot parameters
CX 22.80 cm
CY 15.65 cm
F1P 180.000 ppm
F1 22640.47 Hz
F2P 0.000 ppm
F2 0.00 Hz
PPMCM 7.89474 ppm/cm
HZCM 993.00323 Hz/cm

1H spectrum

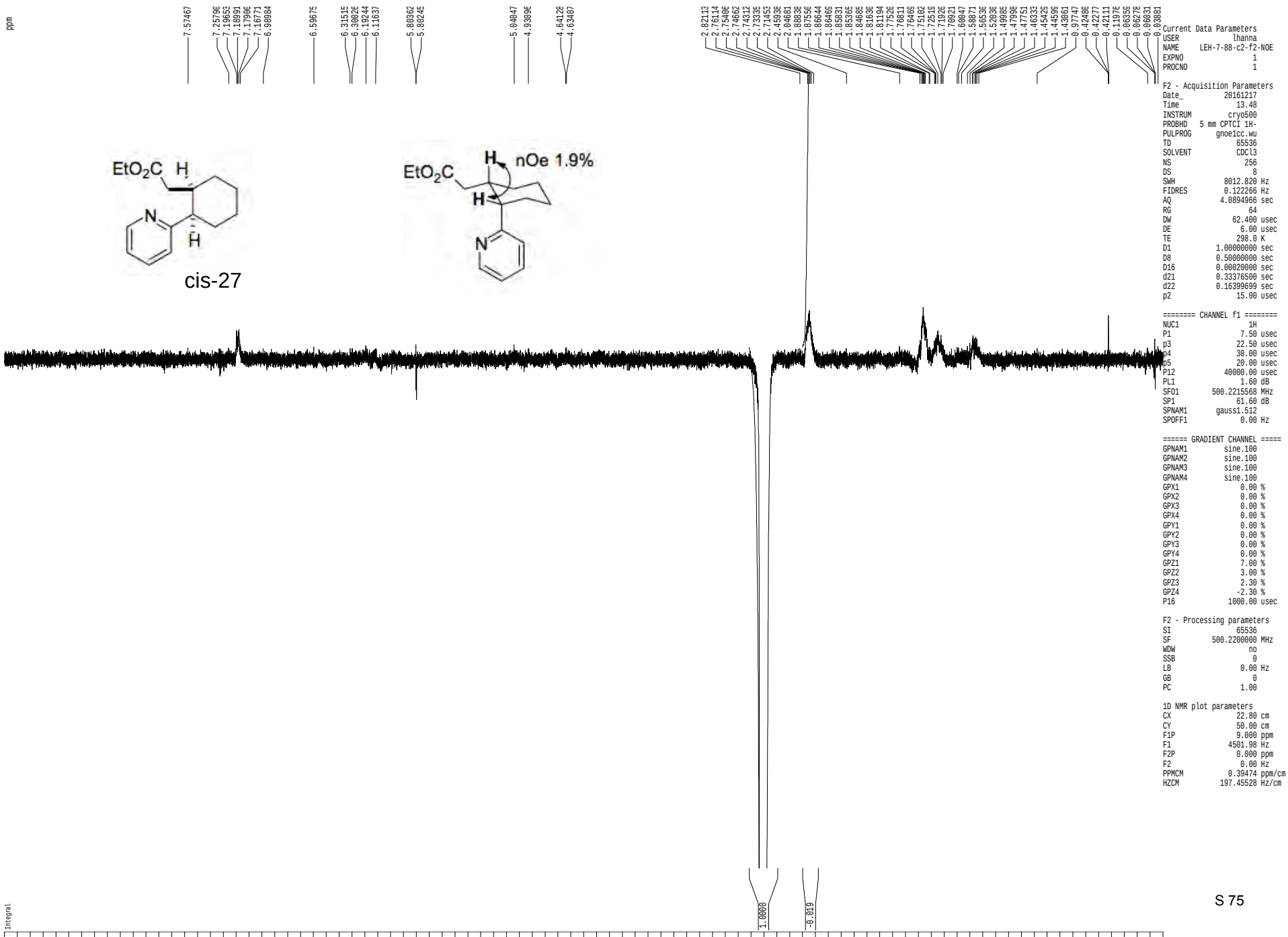


cis-27

Z-restored spin-echo 13C spectrum with 1H decoupling



gnoe

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Current Data Parameters
USER                lhanna
NAME      LEH-7-88-c2-f2-NOE
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_            20161217
Time                13.48
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG        gnoe1cc.wu
TD                  65536
SOLVENT             CDCl3
NS                    256
DS                      8
SWH              8812.820 Hz
FIDRES           0.122266 Hz
AQ               4.0894966 sec
RG                     64
DW                 62.400 usec
DE                  6.00 usec
TE                298.0 K
D1             1.00000000 sec
D8             0.50000000 sec
D16            0.00020000 sec
d21            0.33376500 sec
d22            0.16399699 sec
p2                 15.00 usec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
p3                 22.50 usec
p4                 30.00 usec
p5                 20.00 usec
P12             40000.00 usec
PL1                 1.60 dB
SFO1          500.2215568 MHz
SP1                61.60 dB
SPNAM1         gauss1.512
SPOFF1              0.00 Hz

====== GRADIENT CHANNEL =====
GPNAM1           sine.100
GPNAM2           sine.100
GPNAM3           sine.100
GPNAM4           sine.100
GPX1                0.00 %
GPX2                0.00 %
GPX3                0.00 %
GPX4                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPY3                0.00 %
GPY4                0.00 %
GPZ1                7.00 %
GPZ2                3.00 %
GPZ3                2.30 %
GPZ4               -2.30 %
P16              1000.00 usec

F2 - Processing parameters
SI                  65536
SF            500.2200000 MHz
WDW                    no
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   1.00

1D NMR plot parameters
CX                  22.80 cm
CY                  50.00 cm
F1P                 9.000 ppm
F1                4501.98 Hz
F2P                 0.000 ppm
F2                   0.00 Hz
PPMCM            0.39474 ppm/cm
HZCM           197.45528 Hz/cm
```