

Enantioselective Hydroacylation of *N*-Vinylindole-2-carboxaldehydes

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Supporting Information

Table of Contents

General Experimental Details	S-1
Materials	S-2
General Procedure for Synthesis of Compounds S3a-n	S-3
Characterization Data for Compounds S3a-n	S-4
General Procedure for Synthesis of <i>N</i> -Vinylindole-2-carboxaldehydes 1a-n	S-8
Characterization Data for <i>N</i> -Vinylindole-2-carboxaldehydes 1a-n	S-8
General Procedure for Synthesis of 2,3-Dihydro-1 <i>H</i> -pyrrolo[1,2- <i>a</i>]indol-1-ones 2a-n	S-12
Characterization Data for 2,3-Dihydro-1 <i>H</i> -pyrrolo[1,2- <i>a</i>]indol-1-ones 2a-n	S-13
Procedures for Synthesis of 2a at 0.2 and 1 mol % Catalyst Loading	S-18
Synthesis of (<i>S</i>)-9-Bromo-3-phenyl-2,3-dihydro-1 <i>H</i> -pyrrolo[1,2- <i>a</i>]indol-1-one 3	S-19
Absolute Stereochemistry and Structure of 3	S-19
¹ H, ¹³ C, and ¹⁹ F NMR Spectra for Compounds S3a-n	S-20
¹ H, ¹³ C, and ¹⁹ F NMR Spectra for <i>N</i> -Vinylindole-2-carboxaldehydes 1a-n	S-51
¹ H, ¹³ C, and ¹⁹ F NMR Spectra and HPLC Traces for Compounds 2a-n	S-82
¹ H and ¹³ C NMR Spectra for Compound 3	S-141

General Experimental Details

All air-sensitive procedures were conducted under inert atmosphere in a nitrogen-filled dry box or by standard Schlenk techniques. All reactions were performed under an atmosphere of nitrogen unless otherwise stated. All glassware for moisture sensitive reactions was dried at 140 °C in an oven. THF and CH₂Cl₂ were degassed by purging with argon for 45 minutes and dried with a solvent purification system by passing through a one-meter column of activated alumina. Anhydrous acetonitrile, toluene, 1,2-dichloroethane and 1,4-dioxane were purchased from Aldrich. Flash column chromatography was performed on Fisher brand silica gel 60 (230-400 mesh) using hexanes/EtOAc, hexanes/ether or hexanes/dichloromethane mixtures. Reaction products were visualized on TLC by UV light or by staining with KMnO₄ or 2,4-dinitro-phenylhydrazine.

HRMS (EI) analysis was performed at the Iowa State University Chemical Instrumentation Facility on a Waters GCT GC-MS spectrometer. Optical rotations were measured on an Atago AP-300 automatic polarimeter. HPLC analyses were carried out on a Water Alliance HPLC system with an e2695 Separations Module and a 2489 (UV/Vis) dual wavelength detector. NMR spectra were acquired on Varian MR-400 and Bruker Avance III 600 spectrometers at the Iowa State University Chemical Instrumentation Facility. Chemical shifts are reported in ppm relative to a residual solvent peak (CDCl_3 = 7.26 ppm for ^1H and 77.36 ppm for ^{13}C ; C_6D_6 = 7.16 for ^1H and 128.06 for ^{13}C). ^{19}F NMR shifts are reported in ppm relative to trifluoroacetic acid as an external standard ($\text{F}_3\text{CCO}_2\text{H}$ = -76.55 ppm). Coupling constants are reported in hertz.

Materials

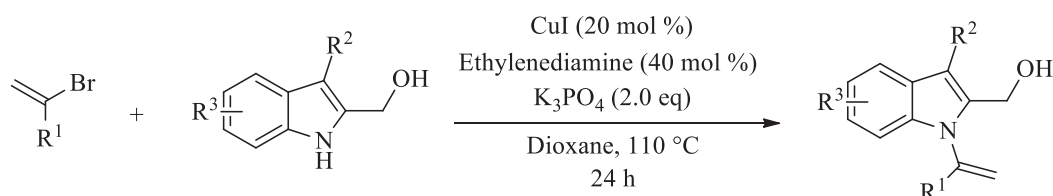
(1-Bromovinyl)benzene **S1a** was purchased from Sigma-Aldrich and used without further purification. 1-(1-Bromovinyl)-4-methoxybenzene **S1b**, 1-(1-bromovinyl)-4-chlorobenzene **S1c**, 1-(1-bromovinyl)-4-(trifluoromethyl)benzene **S1d**, 1-(1-bromovinyl)-3-methoxybenzene **S1e**, 5-(1-bromovinyl)-1,2,3-trimethoxybenzene **S1f**, and (1-bromovinyl)cyclohexane were prepared according to a previously reported procedure.¹ 2-Bromopropene was purchased from Alfa-Aesar and used without further purification. Ethyl indole-2-carboxylate, ethyl 5-methoxyindole-2-carboxylate, and ethyl 5-fluoroindole-2-carboxylate were purchased from AK Scientific and used without further purification. Ethyl 3-ethylindole-2-carboxylate, ethyl 4-methoxyindole-2-carboxylate, ethyl 6-chloroindole-2-carboxylate, ethyl 6-trifluoromethylindole-2-carboxylate were synthesized according to a literature procedure.² (1*H*-Indol-2-yl)methanols **S2a-g** by reduction of the corresponding ethyl indole-2-carboxylate with LiAlH_4 .³ Manganese dioxide, copper iodide, ethylenediamine and Martin Sulfurane were purchased from Sigma-Aldrich and used without further purification. $[\text{Rh}(\text{COD})\text{Cl}]_2$, (*R*)-BINAP, *rac*-BINAP, (*R*)-tolyl-BINAP, (*R*)-xylyl-BINAP, (*S*)-Me-BIPHEP, (*S*)-MeO-BIPHEP, (*R*)-MeO-BIPHEP, silver nitrate, silver mesylate, silver triflate, silver perchlorate, silver tetrafluoroborate, silver hexafluorophosphate, and silver hexafluoroantimonate were purchased from Strem Chemicals and used without further purification.

¹ A. Spaggiari, D. Vaccari, P. Davoli, G. Torre, F. Prati, *J. Org. Chem.*, 2007, **72**, 2216.

² a) K. Ando, K. Yamada, *Tetrahedron Lett.*, 2010, **51**, 3297; b) V. Nair, T. G. George, *Tetrahedron Lett.*, 2000, **41**, 3199; c) J. S. Sawyer, E. C. R. Smith, *PCT Int. Appl., WO 2001081306*, 2001.

³ J. An, N. J. Chang, L. D Song, Y. Q. Jin, Y. Ma, J. R. Chen, W. J. Xiao, *Chem. Commun.*, 2011, **47**, 1869.

General Procedure for Synthesis of (1-(1-Arylviny)-1*H*-indol-2-yl)methanols (S3a-f, S3i-n) and (1-(1-Alkylviny)-1*H*-indol-2-yl)methanols (S3g-h)



S1a; R¹ = Ph

S1b; R¹ = 4-MeO-C₆H₄

S1c; R¹ = 4-Cl-C₆H₄

S1d; R¹ = 4-F₃C-C₆H₄

S1e; R¹ = 3-MeO-C₆H₄

S1f; R¹ = 3,4,5-MeO₃-C₆H₂

S1g; R¹ = Me

S1h; R¹ = C₆H₁₁

S2a; R² = H, R³ = H

S2b; R² = C₂H₅, R³ = H

S2c; R² = H, R³ = 4-MeO

S2d; R² = H, R³ = 5-MeO

S2e; R² = H, R³ = 5-F

S2f; R² = H, R³ = 6-Cl

S2g; R² = H, R³ = 6-F₃C

S3a; R¹ = Ph, R² = H, R³ = H

S3b; R¹ = 4-MeO-C₆H₄, R² = H, R³ = H

S3c; R¹ = 4-Cl-C₆H₄, R² = H, R³ = H

S3d; R¹ = 4-F₃C-C₆H₄, R² = H, R³ = H

S3e; R¹ = 3-MeO-C₆H₄, R² = H, R³ = H

S3f; R¹ = 3,4,5-MeO₃-C₆H₂, R² = H, R³ = H

S3g; R¹ = Me, R² = H, R³ = H

S3h; R¹ = C₆H₁₁, R² = H, R³ = H

S3i; R¹ = Ph, R² = C₂H₅, R³ = H

S3j; R¹ = Ph, R² = H, R³ = 4-MeO

S3k; R¹ = Ph, R² = H, R³ = 5-MeO

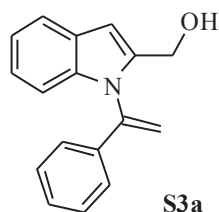
S3l; R¹ = Ph, R² = H, R³ = 5-F

S3m; R¹ = Ph, R² = H, R³ = 6-Cl

S3n; R¹ = Ph, R² = H, R³ = 6-F₃C

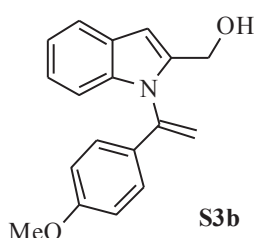
(1-(1-Arylviny)-1*H*-indol-2-yl)methanols (**S3a-f**, **S3i-n**) and (1-(1-alkylviny)-1*H*-indol-2-yl)methanols (**S3g-h**) were prepared according to a modified literature procedure from the appropriate vinyl bromides **S1a-h** and (1*H*-indol-2-yl)methanols **S2a-g**.⁴ In a nitrogen-filled glovebox, to a 20 mL scintillation vial or a 250 mL pressure vessel equipped with a vacuum valve were added CuI (0.200 equiv), the appropriate (1*H*-indol-2-yl)methanol **S2a-g** (1.20 equiv), K₃PO₄ (2.00 equiv), the appropriate vinyl bromide **S1a-h** (1.00 equiv), ethylenediamine (0.400 equiv), and 1,4-dioxane (0.55 M final concentration of vinyl bromides **S1a-h**). The scintillation vial or pressure vessel was sealed with a teflon-lined septum cap or a PTFE stopper. The reaction vessel was removed from the glovebox, and the reaction mixture was stirred at 110 °C for 24 h. The reaction mixture was cooled to room temperature, diluted with EtOAc, and stirred for an addition 15 min. Solids were removed by filtration and washed with EtOAc (3x). The organic layers were combined and concentrated under reduced pressure. The crude product was purified by flash column silica gel chromatography (hexane:EtOAc) to give the appropriate (1-(1-arylviny)-1*H*-indol-2-yl)methanol (**S3a-f**, **S3i-n**) and (1-(1-alkylviny)-1*H*-indol-2-yl)methanol (**S3g-h**).

⁴ Q. Liao, Y. Wang, L. Zhang, C. Xi, *J. Org. Chem.*, 2009, **74**, 6371.



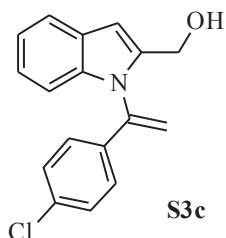
S3a

(1-(1-Phenylvinyl)-1H-indol-2-yl)methanol (S3a): Prepared according to the general procedure from **S1a** (5.00 g, 27.3 mmol) and **S2a** (4.82 g, 32.8 mmol). The mixture was purified by flash column chromatography (80:20 hexane:EtOAc) to give **S3a** as a yellow oil in 65% yield (4.42 g, 17.7 mmol). ¹H NMR (400 MHz, CDCl₃) δ 7.63 – 7.55 (m, 1H), 7.32 – 7.04 (m, 8H), 6.60 (s, 1H), 6.00 (s, 1H), 5.46 (s, 1H), 4.54 (s, 2H), 1.62 (s, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 142.9, 139.9, 138.6, 137.1, 129.5, 129.1, 127.9, 126.0, 122.7, 121.0, 120.6, 114.1, 111.3, 103.1, 57.8. HRMS (EI): Calcd. for C₁₇H₁₅NO ([M]⁺): 249.1154, Found: 249.1149.



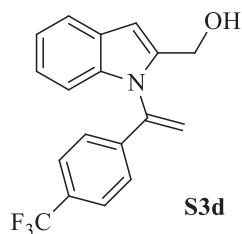
S3b

(1-(1-(4-Methoxyphenyl)vinyl)-1H-indol-2-yl)methanol (S3b): Prepared according to the general procedure from **S1b** (1.95 g, 9.15 mmol) and **S2a** (1.62 g, 11.0 mmol). The mixture was purified by flash column chromatography (80:20 hexane: EtOAc) to give **S3b** as a light yellow solid in 37% yield (0.950 g, 3.40 mmol). ¹H NMR (400 MHz, CDCl₃) δ 7.70 – 7.62 (m, 1H), 7.28 – 7.06 (m, 5H), 6.84 – 6.78 (m, 2H), 6.65 (s, 1H), 5.93 (s, 1H), 5.40 (s, 1H), 4.61 (s, 2H), 3.78 (s, 3H), 1.77 (br s, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 160.6, 142.5, 140.0, 138.6, 129.6, 127.8, 127.4, 122.6, 120.9, 120.5, 114.4, 112.0, 111.4, 102.9, 57.8, 55.6. HRMS (EI): Calcd. for C₁₈H₁₇NO₂ ([M]⁺): 279.1259, Found: 279.1259.



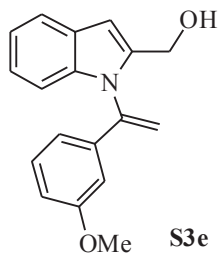
S3c

(1-(1-(4-Chlorophenyl)vinyl)-1H-indol-2-yl)methanol (S3c): Prepared according to the general procedure from **S1c** (1.50 g, 6.90 mmol) and **S2a** (1.22 g, 8.28 mmol). The mixture was purified by flash column chromatography (80:20 hexanes:EtOAc) to give **S3c** as a light yellow oil in 20% yield (0.400 g, 1.41 mmol). ¹H NMR (400 MHz, CDCl₃) δ 7.93 – 7.83 (m, 1H), 7.52 – 7.45 (m, 2H), 7.42 – 7.26 (m, 5H), 6.88 (s, 1H), 6.27 (d, *J* = 1.4 Hz, 1H), 5.76 (d, *J* = 1.4 Hz, 1H), 4.84 (s, 2H), 1.89 (br s, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 142.0, 139.8, 138.5, 135.6, 135.4, 129.3, 127.9, 127.4, 122.9, 121.1, 120.8, 114.6, 111.3, 103.4, 57.8. HRMS (EI): Calcd. for C₁₇H₁₄ClNO ([M]⁺): 283.0764, Found: 283.0760.

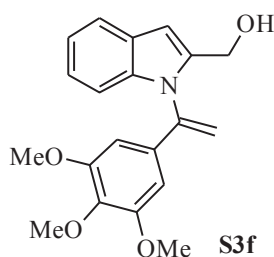


S3d

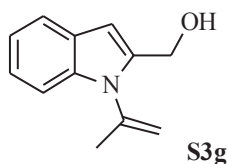
(1-(1-(4-(Trifluoromethyl)phenyl)vinyl)-1H-indol-2-yl)methanol (S3d): Prepared according to the general procedure from **S1d** (2.00 g, 7.97 mmol) and **S2a** (1.41 g, 9.56 mmol). The mixture was purified by flash column chromatography (80:20 hexane:EtOAc) to give **S3d** as a dark yellow oil in 17% yield (0.425 g, 1.34 mmol). ¹H NMR (400 MHz, C₆D₆) δ 7.68 (dq, *J* = 8.0, 1.2, 0.80 Hz, 1H), 7.22 – 7.01 (m, 5H), 6.79 – 6.69 (m, 2H), 6.51 (q, *J* = 1.2, 0.40 Hz, 1H), 5.45 (s, 1H), 5.11 (s, 1H), 4.21 (d, *J* = 5.6 Hz, 2H), 0.43 (s, 1H). ¹³C NMR (101 MHz, C₆D₆) δ 141.8, 140.5, 140.1, 138.7, 130.9, 130.6, 126.4, 125.9, 125.8, 125.8, 125.8, 123.0, 121.3, 121.1, 115.8, 111.2, 103.3, 57.3. ¹⁹F NMR (CDCl₃, 376 MHz): δ -63.0. HRMS (EI): Calcd. for C₁₈H₁₄F₃NO ([M]⁺): 317.1027, Found: 317.1030.



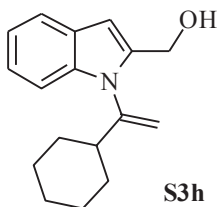
(1-(1-(3-Methoxyphenyl)vinyl)-1H-indol-2-yl)methanol (S3e): Prepared according to the general procedure from **S1e** (1.95 g, 9.15 mmol) and **S2a** (1.62 g, 11.0 mmol). The mixture was purified by flash column chromatography (80:20 hexane:EtOAc) to give **S3e** as a light yellow solid in 15% yield (0.260 g, 0.930 mmol). ¹H NMR (400 MHz, CDCl₃) δ 7.78 – 7.70 (m, 1H), 7.38 – 6.20 (m, 4H), 6.98 (dd, *J* = 8.4, 1.6 Hz, 1H), 6.89 – 6.79 (m, 2H), 6.77 – 6.74 (m, 1H), 6.15 (s, 1H), 5.63 (s, 1H), 4.71 (s, 2H), 3.84 (s, 3H), 1.79 (br s, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 160.2, 142.8, 139.9, 138.7, 130.2, 127.9, 122.7, 121.0, 120.6, 118.6, 114.7, 114.4, 111.9, 111.3, 103.1, 57.8, 55.6. HRMS (EI): Calcd. for C₁₈H₁₇NO₂ ([M]⁺): 279.1259, Found: 279.1249.



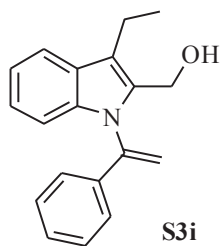
(1-(1-(3,4,5-Trimethoxyphenyl)vinyl)-1H-indol-2-yl)methanol (S3f): Prepared according to the general procedure from **S1f** (1.150 g, 4.210 mmol) and **S2a** (0.744 g, 5.05 mmol). The mixture was purified by flash column chromatography (70:30 hexane:EtOAc) to give **S3f** as a light yellow solid in 12% yield (0.170 g, 0.500 mmol). ¹H NMR (400 MHz, CDCl₃) δ 7.67 – 7.58 (m, 1H), 7.25 – 7.06 (m, 3H), 6.64 (s, 1H), 6.38 (s, 2H), 5.96 (s, 1H), 5.47 (s, 1H), 4.62 (s, 2H), 3.84 (s, 3H), 3.70 (s, 6H), 1.63 (br s, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 153.7, 142.9, 140.0, 139.3, 138.8, 132.9, 127.8, 122.7, 121.0, 120.6, 113.4, 111.3, 103.4, 103.2, 61.2, 57.8, 56.4. HRMS (EI): Calcd. for C₂₀H₂₁NO₄ ([M]⁺): 339.1471, Found: 339.1484.



(1-(Prop-1-en-2-yl)-1H-indol-2-yl)methanol (S3g): Prepared according to the general procedure from **S1g** (1.50 g, 12.4 mmol) and **S2a** (2.19 g, 14.9 mmol). The mixture was purified by flash column chromatography (80:20 hexane:ethylacetate) to give **S3g** as a light yellow solid in 52% yield (1.22 g, 6.49 mmol). ¹H NMR (400 MHz, CDCl₃) δ 7.33 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.06 (dd, *J* = 8.0, 0.4 Hz, 1H), 6.90 (dddd, *J* = 36.4, 15.2, 7.2, 1.2 Hz, 2H), 6.26 (s, 1H), 5.20 (q, *J* = 2.8, 1.2 Hz, 1H), 4.93 (s, 1H), 4.48 (s, 2H), 1.91 (s, 3H), 1.56 (br s, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 141.1, 138.8, 137.4, 127.8, 122.5, 121.0, 120.3, 115.9, 110.8, 102.5, 57.7, 22.2. HRMS (EI): Calcd. for C₁₂H₁₃NO ([M]⁺): 187.0997, Found: 187.1004.

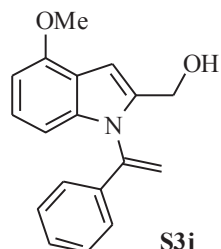


(1-(1-Cyclohexylvinyl)-1H-indol-2-yl)methanol (S3h): Prepared according to the general procedure from **S1h** (1.70 g, 8.99 mmol) and **S2a** (1.59 g, 10.8 mmol). The mixture was purified by flash column chromatography (80:20 hexane:EtOAc) to give **S3h** as a light yellow oil in 9% yield (0.210 g, 0.822 mmol). ¹H NMR (400 MHz, CDCl₃) δ 7.75 – 7.67 (m, 1H), 7.45 – 7.35 (m, 1H), 7.27 (dddd, *J* = 30.0, 15.2, 8.4, 7.2, 1.2 Hz, 2H), 6.69 (q, *J* = 1.6, 0.40 Hz, 1H), 5.57 (d, *J* = 1.6 Hz, 1H), 5.35 (d, *J* = 0.40 Hz, 1H), 4.85 (s, 2H), 2.57 – 2.50 (m, 1H), 1.97 – 1.76 (m, 6H), 1.49 – 1.21 (m, 5H). ¹³C NMR (101 MHz, CDCl₃) δ 150.0, 139.7, 138.1, 127.7, 122.3, 120.9, 120.2, 113.4, 111.3, 102.2, 57.9, 43.6, 31.9, 26.6, 26.4. HRMS (EI): Calcd. for C₁₇H₂₁NO ([M]⁺): 255.1623, Found: 255.1627.



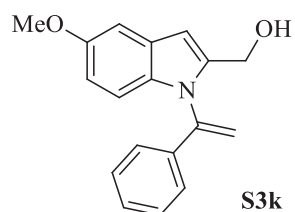
S3i

(3-Ethyl-1-(1-phenylvinyl)-1H-indol-2-yl)methanol (S3i): Prepared according to the general procedure from **S1a** (0.800 g, 4.37 mmol) and **S2b** (0.919 g, 5.24 mmol). The mixture was purified by flash column chromatography (80:20 hexane:EtOAc) to give **S3i** as a light yellow solid in 30% yield (0.370 g, 1.33 mmol). ^1H NMR (400 MHz, CDCl_3) δ 7.73 – 7.53 (m, 1H), 7.44 – 7.23 (m, 3H), 7.25 – 7.08 (m, 5H), 6.06 (s, 1H), 5.54 (s, 1H), 4.61 (s, 2H), 2.89 (q, J = 15.2, 7.6 Hz, 2H), 1.36 – 1.32 (t, J = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 143.2, 137.9, 137.6, 134.8, 129.5, 129.2, 127.6, 126.1, 123.0, 120.0, 119.5, 118.7, 114.2, 111.3, 54.9, 18.0, 16.7. HRMS (EI): Calcd. for $\text{C}_{19}\text{H}_{19}\text{NO}$ ($[\text{M}]^+$): 277.1467, Found: 277.1469.



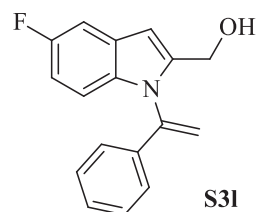
S3j

(4-Methoxy-1-(1-phenylvinyl)-1H-indol-2-yl)methanol (S3j): Prepared according to the general procedure from **S1a** (0.900 g, 4.92 mmol) and **S2c** (1.05 g, 5.90 mmol). The mixture was purified by flash column chromatography (80:20 hexane:EtOAc) to give **S3j** as a light yellow solid in 51% yield (0.700 g, 2.51 mmol). ^1H NMR (400 MHz, CDCl_3) δ 7.24 – 7.04 (m, 3H), 6.90 (dt, J = 8.4, 2.0 Hz, 3H), 6.67 – 6.57 (m, 2H), 6.39 (dd, J = 7.6, 0.80 Hz, 1H), 5.87 (d, J = 1.6 Hz, 1H), 5.35 (d, J = 1.6 Hz, 1H), 4.40 (s, 2H), 3.81 (d, J = 1.2 Hz, 3H), 1.67 (br s, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 153.2, 142.7, 139.7, 138.3, 137.1, 136.8, 136.0, 129.2, 128.8, 128.5, 127.4, 126.1, 125.7, 124.1, 124.0, 123.2, 121.6, 118.1, 113.9, 104.9, 104.5, 101.9, 101.0, 100.2, 57.4, 55.4. HRMS (EI): Calcd. for $\text{C}_{18}\text{H}_{17}\text{NO}_2$ ($[\text{M}]^+$): 279.1259, Found: 279.1272.



S3k

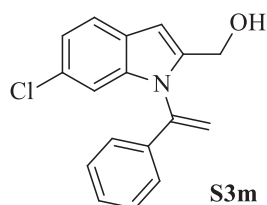
(5-Methoxy-1-(1-phenylvinyl)-1H-indol-2-yl)methanol (S3k): Prepared according to the general procedure from **S1a** (1.30 g, 7.10 mmol) and **S2d** (1.51 g, 8.52 mmol). The mixture was purified by flash column chromatography (80:20 hexane:EtOAc) to give **S3k** as a light yellow solid in 29% yield (0.568 g, 2.03 mmol). ^1H NMR (400 MHz, CDCl_3) δ 7.26 – 7.09 (m, 3H), 7.05 – 6.86 (m, 4H), 6.65 (dd, J = 8.8, 2.0 Hz, 1H), 6.43 (s, 1H), 5.86 (s, 1H), 5.35 (s, 1H), 4.43 (s, 2H), 3.71 (s, 3H), 1.66 (br s, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 154.8, 143.0, 140.5, 137.2, 133.8, 129.5, 129.1, 128.2, 126.1, 113.8, 112.8, 112.1, 102.8, 102.6, 57.8, 56.1. HRMS (EI): Calcd. for $\text{C}_{18}\text{H}_{17}\text{NO}_2$ ($[\text{M}]^+$): 279.1259, Found: 279.1267.



S3l

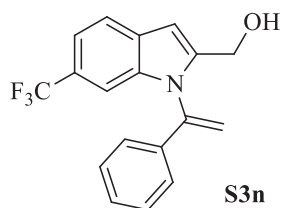
5-Fluoro-1-(1-phenylvinyl)-1H-indol-2-yl)methanol (S3l): Prepared according to the general procedure from **S1a** (0.688 g, 3.76 mmol) and **S2e** (0.745 g, 4.51 mmol). The mixture was purified by flash column chromatography (80:20 hexane:EtOAc) to give **S3l** as a light yellow solid in 55% yield (0.551 g, 2.06 mmol). ^1H NMR (400 MHz, CDCl_3) δ 7.25 – 7.06 (m, 4H), 6.96 – 6.90 (m, 2H), 6.86 (dd, J = 9.2, 4.4 Hz, 1H), 6.67

(tdd, $J = 9.2, 2.4, 0.80$ Hz, 1H), 6.40 (s, 1H), 5.84 (s, 1H), 5.30 (s, 1H), 4.38 (s, 2H), 1.69 (br s, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 159.7, 157.3, 142.8, 141.5, 136.8, 135.1, 129.6, 129.2, 128.2, 128.1, 126.0, 114.2, 112.1, 112.0, 111.2, 110.9, 105.9, 105.6, 102.9, 102.9, 57.8. ^{19}F NMR (CDCl_3 , 376 MHz): δ -124.5. HRMS (EI): Calcd. for $\text{C}_{17}\text{H}_{14}\text{FNO}$ ($[\text{M}]^+$): 267.1059, Found: 267.1068.



S3m

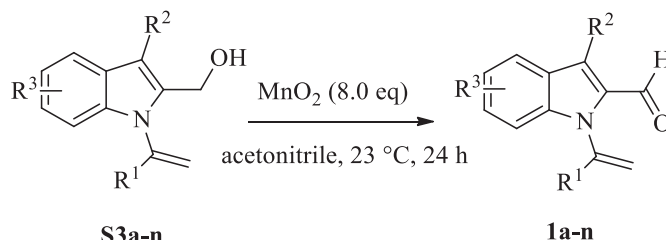
(6-Chloro-1-(1-phenylvinyl)-1H-indol-2-yl)methanol (S3m): Prepared according to the general procedure from **S1a** (1.95 g, 10.6 mmol) and **S2f** (2.32 g, 12.8 mmol). The mixture was purified by flash column chromatography (80:20 hexane:EtOAc) to give **S3m** as a light yellow oil in 53% yield (1.60 g, 5.64 mmol). ^1H NMR (400 MHz, C_6D_6) δ 7.40 – 7.35 (m, 2H), 7.18 – 7.16 (m, 3H), 6.98 – 6.82 (m, 3H), 6.43 (s, 1H), 5.44 (s, 1H), 4.95 (s, 1H), 4.20 (s, 2H), 1.65 (s, 1H). ^{13}C NMR (101 MHz, C_6D_6) δ 142.4, 141.3, 139.3, 136.8, 129.3, 129.0, 125.9, 122.0, 121.6, 114.1, 111.3, 102.7, 57.5. HRMS (EI): Calcd. for $\text{C}_{17}\text{H}_{14}\text{ClNO}$ ($[\text{M}]^+$): 283.0764, Found: 283.0762.



S3n

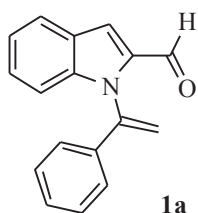
(1-(1-Phenylvinyl)-6-(trifluoromethyl)-1H-indol-2-yl)methanol (S3n): Prepared according to the general procedure from **S1a** (1.20 g, 6.56 mmol) and **S2g** (1.69 g, 7.87 mmol). The mixture was purified by flash column chromatography (80:20 hexane:EtOAc) to give **S3n** as a light yellow oil in 30% yield (0.620 g, 1.95 mmol). ^1H NMR (400 MHz, C_6D_6) δ 7.69 (s, 1H), 7.53 – 7.39 (m, 2H), 6.97 – 6.76 (m, 5H), 6.49 (s, 1H), 5.43 (s, 1H), 4.92 (s, 1H), 4.19 (s, 2H), 1.44 (br s, 1H). ^{13}C NMR (101 MHz, C_6D_6) δ 143.3, 142.2, 137.8, 136.5, 130.7, 129.4, 129.0, 127.4, 125.8, 125.2, 124.9, 124.7, 124.6, 124.3, 121.5, 117.4, 114.3, 108.6, 102.5, 57.5. ^{19}F NMR (CDCl_3 , 376 MHz): δ -60.7. HRMS (EI): Calcd. for $\text{C}_{18}\text{H}_{14}\text{F}_3\text{NO}$ ($[\text{M}]^+$): 317.1027, Found: 317.1023.

General Procedure for Synthesis of 1-(1-Arylvinyl)-1*H*-indole-2-carbaldehydes (1a-f**, **1i-n**) and 1-(1-Alkylvinyl)-1*H*-indole-2-carboxaldehydes (**1g-h**)**

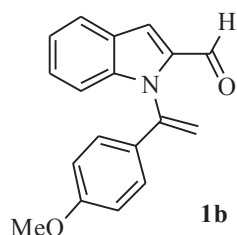


- 1a**; R¹ = Ph, R² = H, R³ = H
1b; R¹ = 4-MeO-C₆H₄, R² = H, R³ = H
1c; R¹ = 4-Cl-C₆H₄, R² = H, R³ = H
1d; R¹ = 4-F₃C-C₆H₄, R² = H, R³ = H
1e; R¹ = 3-MeO-C₆H₄, R² = H, R³ = H
1f; R¹ = 3,4,5-MeO₃-C₆H₂, R² = H, R³ = H
1g; R¹ = Me, R² = H, R³ = H
1h; R¹ = C₆H₁₁, R² = H, R³ = H
1i; R¹ = Ph, R² = C₂H₅, R³ = H
1j; R¹ = Ph, R² = H, R³ = 4-MeO
1k; R¹ = Ph, R² = H, R³ = 5-MeO
1l; R¹ = Ph, R² = H, R³ = 5-F
1m; R¹ = Ph, R² = H, R³ = 6-Cl
1n; R¹ = Ph, R² = H, R³ = 6-F₃C

To an acetonitrile solution (0.40 M) of the appropriate 1-(1-arylvinyl)-1*H*-indol-2-yl)methanol (**S3a-f**, **S3i-n**) or 1-(1-alkylvinyl)-1*H*-indol-2-yl)methanol (**S3g-h**) (1.00 equiv) in a round-bottom flask was manganese dioxide (8.00 equiv) added. The reaction mixture was stirred at room temperature under N₂ atmosphere for 24 hours. The reaction mixture was filtered through celite, washed with mixture of hexane:EtOAc (60:40), and the filtrate was concentrated under reduced pressure. The crude product was purified by flash column silica gel chromatography (hexane:EtOAc) to give the appropriate 1-(1-arylvinyl)-1*H*-indole-2-carboxaldehydes (**1a-f**, **1i-n**) or 1-(1-alkylvinyl)-1*H*-indole-2-carboxaldehydes (**1g-h**).

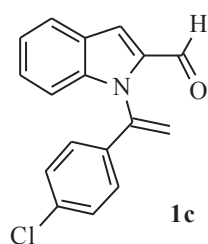


1-(1-Phenylvinyl)-1*H*-indole-2-carboxaldehyde (1a**):** Prepared according to the general procedure from **S3a** (5.00 g, 20.1 mmol). The mixture was purified by flash column chromatography (90:10 hexane:EtOAc) to give **1a** as a light yellow solid in 85% yield (4.20 g, 17.0 mmol). ¹H NMR (400 MHz, CDCl₃) δ 9.72 (d, *J* = 1.2 Hz, 1H), 7.72 (dq, *J* = 8.4, 1.6, 0.80 Hz, 1H), 7.35 (q, *J* = 1.2, 0.8 Hz, 1H), 7.33 – 7.25 (m, 2H), 7.24 – 7.12 (m, 3H), 7.06 – 7.00 (m, 2H), 6.02 (d, *J* = 0.4 Hz, 1H), 5.41 (d, *J* = 0.4 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 181.7, 143.1, 141.0, 137.3, 136.7, 129.4, 129.0, 127.5, 126.8, 125.7, 123.6, 122.1, 115.7, 113.9, 112.1. HRMS (EI): Calcd. for C₁₇H₁₃NO ([M]⁺): 247.0997, Found: 247.1006.



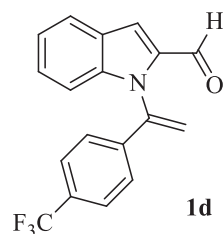
1-(1-(4-Methoxyphenyl)vinyl)-1H-indole-2-carboxaldehyde (1b):

Prepared according to the general procedure from **S3b** (0.958 g, 3.43 mmol). The mixture was purified by flash column chromatography (90:10 hexane:EtOAc) to give **1b** as a light yellow solid in 80% yield (0.760 g, 2.740 mmol). ¹H NMR (400 MHz, CDCl₃) δ 9.87 (s, 1H), 7.84 (dt, *J* = 8.0, 0.80 Hz, 1H), 7.47 (d, *J* = 0.80, 1H), 7.45 – 7.37 (m, 2H), 7.32 – 7.23 (m, 1H), 7.16 – 7.07 (m, 2H), 6.88 – 6.80 (m, 2H), 6.03 (s, 1H), 5.42 (s, 1H), 3.79 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 181.6, 160.4, 142.4, 140.8, 136.6, 129.7, 127.3, 126.9, 126.6, 123.4, 121.9, 115.1, 114.2, 112.0, 111.8, 55.4. HRMS (EI): Calcd. for C₁₈H₁₅NO₂ ([M]⁺): 277.1103, Found: 277.1112.



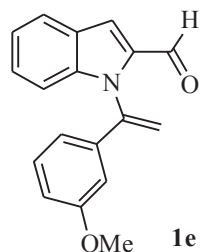
1-(1-(4-Chlorophenyl)vinyl)-1H-indole-2-carboxaldehyde (1c):

Prepared according to the general procedure from **S3c** (0.373 g, 1.31 mmol). The mixture was purified by flash column chromatography (90:10 hexane:EtOAc) to give **1c** as a light yellow solid in 80% yield (0.295g, 1.05 mmol). ¹H NMR (400 MHz, CDCl₃) δ 9.67 (s, 1H), 7.69 (dt, *J* = 8.0, 1.2 Hz, 1H), 7.36 – 7.22 (m, 3H), 7.22 – 7.07 (m, 3H), 6.97 – 6.88 (m, 2H), 5.95 (s, 1H), 5.38 (s, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 181.4, 142.2, 141.0, 136.5, 135.9, 135.2, 129.3, 127.7, 127.0, 126.8, 123.7, 122.2, 116.7, 114.2, 111.9. HRMS (EI): Calcd. for C₁₇H₁₂ClNO ([M]⁺): 281.0607, Found: 281.0600.



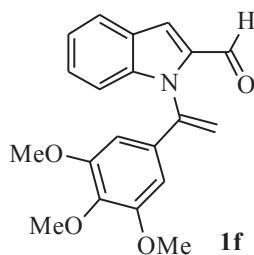
1-(1-(4-(Trifluoromethyl)phenyl)vinyl)-1H-indole-2-carboxaldehyde (1d):

Prepared according to the general procedure from **S3d** (0.425 g, 1.34 mmol). The mixture was purified by flash column chromatography (90:10 hexane:EtOAc) to give **1d** as a light yellow solid in 80% yield (0.339 g, 1.08 mmol). ¹H NMR (400 MHz, CDCl₃) δ 9.70 (s, 1H), 7.74 (dt, *J* = 8.0, 0.80 Hz, 1H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.40 – 7.26 (m, 3H), 7.18 – 7.13 (m, 1H), 7.10 (d, *J* = 8.4 Hz, 2H), 6.09 (s, 1H), 5.52 (s, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 181.3, 142.2, 141.1, 140.8, 136.4, 131.5, 131.2, 130.8, 130.5, 127.9, 126.8, 125.9, 125.6, 123.8, 122.8, 122.3, 117.4, 115.8, 111.7. ¹⁹F NMR (CDCl₃, 376 MHz): δ -63.1. HRMS (EI): Calcd. for C₁₈H₁₂F₃NO ([M]⁺): 315.0871, Found: 315.0881.



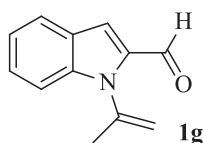
1-(1-(3-Methoxyphenyl)vinyl)-1H-indole-2-carboxaldehyde (1e):

Prepared according to the general procedure from **S3e** (0.147 g, 0.526 mmol). The mixture was purified by flash column chromatography (90:10 hexane:EtOAc) to give **1e** as a light yellow solid in 74% yield (0.108 g, 0.389 mmol). ¹H NMR (400 MHz, CDCl₃) δ 9.68 (s, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.33 – 7.19 (m, 3H), 7.17 – 7.01 (m, 2H), 6.76 – 6.68 (m, 1H), 6.62 – 6.54 (m, 2H), 5.98 (s, 1H), 5.37 (s, 1H), 3.60 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 181.6, 160.1, 142.8, 141.0, 138.7, 136.6, 130.0, 127.4, 126.6, 123.5, 122.0, 118.1, 115.6, 114.4, 114.1, 111.9, 111.6, 55.4. HRMS (EI): Calcd. for C₁₈H₁₅NO₂ ([M]⁺): 277.1103, Found: 277.1111.



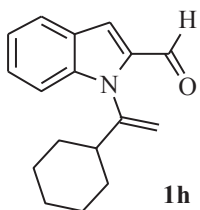
1-(1-(3,4,5-Trimethoxyphenyl)vinyl)-1H-indole-2-carboxaldehyde (1f):

Prepared according to the general procedure from **S3f** (0.170 g, 0.501 mmol). The mixture was purified by flash column chromatography (80:20 hexane:EtOAc) to give **1f** as a light yellow solid in 83% yield (0.140 g, 0.415 mmol). ¹H NMR (400 MHz, CDCl₃) δ 9.53 (d, *J* = 1.6 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.17 – 7.13 (m, 1H), 7.12 – 7.05 (m, 2H), 6.99 – 6.90 (m, 1H), 6.05 (d, *J* = 1.2 Hz, 2H), 5.74 (s, 1H), 5.16 (s, 1H), 3.54 (d, *J* = 1.2 Hz, 3H), 3.41 (d, *J* = 1.2 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 181.7, 153.7, 142.8, 141.1, 139.3, 136.8, 133.0, 127.5, 126.7, 123.6, 122.1, 115.5, 113.3, 112.1, 103.2, 61.2, 56.4. HRMS (EI): Calcd. for C₂₀H₁₉NO₄ ([M]⁺): 337.1314, Found: 337.1303.



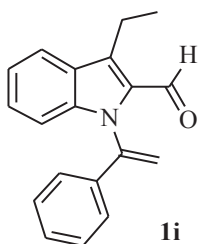
1-(Prop-1-en-2-yl)-1H-indole-2-carboxaldehyde (1g):

Prepared according to the general procedure from **S3g** (1.10 g, 5.87 mmol). The mixture was purified by flash column chromatography (90:10 hexane:EtOAc) to give **1g** as a light yellow solid in 84% yield (0.914g, 4.94 mmol). ¹H NMR (400 MHz, CDCl₃) δ 9.68 (bs, 1H), 7.53 (dq, *J* = 8.0, 2.0, 1.2 Hz, 1H), 7.31 – 7.15 (m, 2H), 7.11 (bs, 1H), 7.00 (ddt, *J* = 7.6, 1.6, 1.2 Hz, 1H), 5.28 (q, *J* = 2.8, 1.2 Hz, 1H), 4.96 (bs, 1H), 1.96 (bs, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 181.5, 141.1, 139.9, 135.7, 127.3, 126.5, 123.3, 121.5, 117.2, 114.6, 111.6, 22.4. HRMS (EI): Calcd. for C₁₂H₁₁NO ([M]⁺): 185.0841, Found: 185.0837.



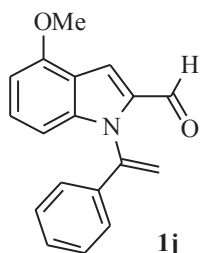
1-(1-Cyclohexylvinyl)-1H-indole-2-carboxaldehyde (1h):

Prepared according to the general procedure from **S3h** (0.253 g, 0.992 mmol). The mixture was purified by flash column chromatography (90:10 hexane:EtOAc) to give **1h** as a light yellow solid in 77% yield (0.193g, 0.763 mmol). ¹H NMR (400 MHz, CDCl₃) δ 9.81 (bs, 1H), 7.64 (dt, *J* = 8.4, 0.80 Hz, 1H), 7.36 – 7.24 (m, 3H), 7.09 (ddd, *J* = 7.6, 6.4, 1.2 Hz, 1H), 5.37 (d, *J* = 1.6 Hz, 1H), 5.11 (bs, 1H), 2.29 – 2.18 (m, 1H), 2.13 – 0.73 (m, 10H). ¹³C NMR (101 MHz, CDCl₃) δ 181.8, 150.0, 141.0, 136.1, 127.1, 126.3, 123.3, 121.5, 116.6, 112.2, 111.9, 44.3, 26.4. HRMS (EI): Calcd. for C₁₇H₁₉NO ([M]⁺): 253.1467, Found: 253.1475.

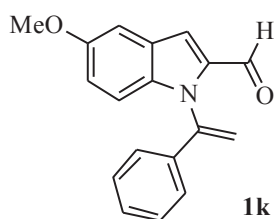


3-Ethyl-1-(1-phenylvinyl)-1H-indole-2-carboxaldehyde (1i):

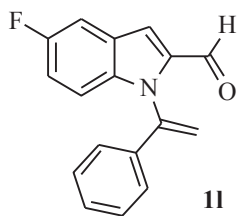
Prepared according to the general procedure from **S3i** (0.260 g, 0.937 mmol). The mixture was purified by flash column chromatography (90:10 hexane:EtOAc) to give **1i** as a light yellow solid in 74% yield (0.192 mg, 0.697 mmol). ¹H NMR (400 MHz, CDCl₃) δ 9.88 (s, 1H), 7.70 (dt, *J* = 8.4, 0.80 Hz, 1H), 7.29 – 7.09 (m, 6H), 7.05 – 6.99 (m, 2H), 5.98 (s, 1H), 5.38 (s, 1H), 3.10 (q, *J* = 7.6 Hz, 2H), 1.30 (t, *J* = 7.6 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 181.5, 143.2, 140.1, 137.5, 132.4, 131.5, 129.3, 129.0, 127.6, 126.8, 125.7, 121.6, 121.3, 113.8, 111.9, 17.9, 16.6. HRMS (EI): Calcd. for C₁₉H₁₇NO ([M]⁺): 275.1310, Found: 275.1323.



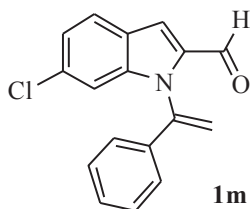
4-Methoxy-1-(1-phenylvinyl)-1H-indole-2-carboxaldehyde (1j): Prepared according to the general procedure from **S3j** (0.490 g, 1.75 mmol). The mixture was purified by flash column chromatography (90:10 hexane:EtOAc) to give **1j** as a light yellow solid in 80% yield (0.390 g, 1.41 mmol). ^1H NMR (400 MHz, CDCl_3) δ 9.71 (s, 1H), 7.45 – 7.42 (m, 1H), 7.20 – 7.12 (m, 4H), 7.03 – 6.98 (m, 2H), 6.86 (dt, J = 8.4, 0.80 Hz, 1H), 6.46 (d, J = 7.6, 1H), 5.96 (d, J = 0.4 Hz, 1H), 5.37 (d, J = 0.4 Hz, 1H), 3.89 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 181.1, 155.3, 143.2, 142.5, 137.2, 135.7, 129.2, 128.9, 128.7, 125.6, 118.4, 114.0, 113.8, 104.6, 100.8, 55.8. HRMS (EI): Calcd. for $\text{C}_{18}\text{H}_{15}\text{NO}_2$ ($[\text{M}]^+$): 277.1103, Found: 277.1091.



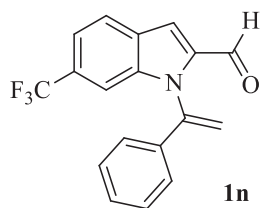
5-Methoxy-1-(1-phenylvinyl)-1H-indole-2-carboxaldehyde (1k): Prepared according to the general procedure from **S3k** (0.500 g, 1.79 mmol). The mixture was purified by flash column chromatography (90:10 hexane:EtOAc) to give **1k** as a light yellow solid in 80% yield (0.400 g, 1.44 mmol). ^1H NMR (400 MHz, CDCl_3) δ 9.76 (s, 1H), 7.34 (d, J = 0.8 Hz, 1H), 7.31 – 7.24 (m, 4H), 7.16 – 7.09 (m, 3H), 7.03 (dd, J = 9.2, 2.4 Hz, 1H), 6.08 (d, J = 0.4 Hz, 1H), 5.48 (d, J = 0.4 Hz, 1H), 3.88 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 181.6, 155.7, 143.1, 137.3, 136.9, 136.5, 129.4, 129.0, 127.1, 125.7, 119.4, 114.6, 113.9, 113.1, 102.9, 56.0. HRMS (EI): Calcd. for $\text{C}_{18}\text{H}_{15}\text{NO}_2$ ($[\text{M}]^+$): 277.1103, Found: 277.1111.



5-Fluoro-1-(1-phenylvinyl)-1H-indole-2-carboxaldehyde (1l): Prepared according to the general procedure from **S3l** (0.515 g, 1.93 mmol). The mixture was purified by flash column chromatography (90:10 hexane:EtOAc) to give **1l** as a light yellow solid in 72% yield (0.367 g, 1.38 mmol). ^1H NMR (400 MHz, CDCl_3) δ 9.79 (s, 1H), 7.42 (dd, J = 8.8, 2.4, 0.4 Hz, 1H), 7.38 (d, J = 0.8 Hz, 1H), 7.34 – 7.24 (m, 4H), 7.16 – 7.07 (m, 3H), 6.11 (d, J = 0.8 Hz, 1H), 5.49 (d, J = 0.8 Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 181.7, 160.1, 157.7, 143.0, 137.7, 137.1, 129.6, 129.1, 126.8, 125.6, 116.8, 116.6, 114.8, 114.2, 113.3, 107.7, 107.5. ^{19}F NMR (CDCl_3 , 376 MHz): δ -121.8. HRMS (EI): Calcd. for $\text{C}_{17}\text{H}_{12}\text{FNO}$ ($[\text{M}]^+$): 265.0903, Found: 265.0896.



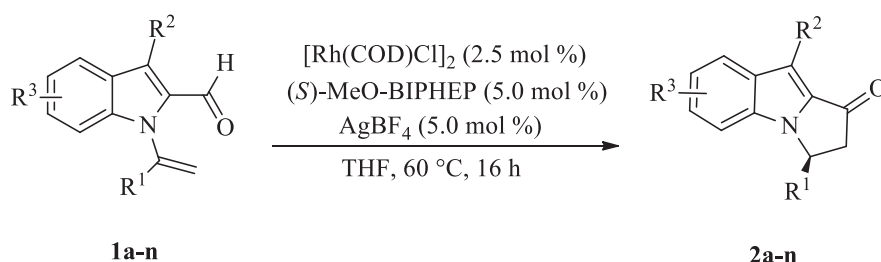
6-Chloro-1-(1-phenylvinyl)-1H-indole-2-carboxaldehyde (1m): Prepared according to the general procedure from **S3m** (1.30 g, 4.58 mmol). The mixture was purified by flash column chromatography (90:10 hexane:EtOAc) to give **1m** as a light yellow solid in 77% yield (1.00 g, 3.55 mmol). ^1H NMR (400 MHz, CDCl_3) δ 9.64 (bs, 1H), 7.58 (dd, J = 8.4, 0.4 Hz, 1H), 7.28 – 7.24 (m, 2H), 7.21 – 7.12 (m, 3H), 7.07 (dd, J = 8.8, 1.6 Hz, 1H), 6.99 – 6.94 (m, 2H), 5.98 (d, J = 0.8 Hz, 1H), 5.36 (d, J = 0.8 Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 181.4, 142.8, 141.3, 137.2, 136.9, 133.6, 129.6, 129.1, 125.6, 125.2, 124.6, 123.3, 115.4, 114.2, 111.9. HRMS (EI): Calcd. for $\text{C}_{17}\text{H}_{12}\text{ClNO}$ ($[\text{M}]^+$): 281.0607, Found: 281.0598.



1-(1-Phenylvinyl)-6-(trifluoromethyl)-1H-indole-2-carboxaldehyde

(1n): Prepared according to the general procedure from **S3n** (0.584 g, 1.84 mmol). The mixture was purified by flash column chromatography (90:10 hexane:EtOAc) to give **1n** as a light yellow solid in 72% yield (0.420 g, 1.33 mmol). ¹H NMR (400 MHz, CDCl₃) δ 9.71 (bs, 1H), 7.78 (d, *J* = 8.4, 1H), 7.63 – 7.57 (m, 1H), 7.38 – 7.30 (m, 2H), 7.23 – 7.11 (m, 3H), 7.02 – 6.94 (m, 2H), 6.04 (bs, 1H), 5.41 (bs, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 181.6, 142.6, 139.7, 138.4, 136.8, 129.7, 129.2, 125.5, 124.4, 118.5, 114.5, 109.7. ¹⁹F NMR (CDCl₃, 376 MHz): δ -61.9. HRMS (EI): Calcd. for C₁₈H₁₂F₃NO ([M]⁺): 315.0871, Found: 315.0862.

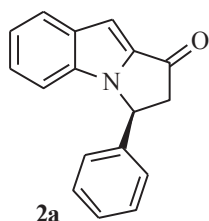
General Procedure for Synthesis of 3-Aryl-2,3-dihydro-1H-pyrrolo[1,2-*a*]indol-1-ones (2a-f, 2i-n) and 3-Alkyl-2,3-dihydro-1H-pyrrolo[1,2-*a*]indol-1-ones (2g-h)



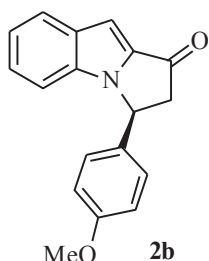
- 2a;** R¹ = Ph, R² = H, R³ = H
2b; R¹ = 4-MeO-C₆H₄, R² = H, R³ = H
2c; R¹ = 4-Cl-C₆H₄, R² = H, R³ = H
2d; R¹ = 4-F₃C-C₆H₄, R² = H, R³ = H
2e; R¹ = 3-MeO-C₆H₄, R² = H, R³ = H
2f; R¹ = 3,4,5-MeO₃-C₆H₂, R² = H, R³ = H
2g; R¹ = Me, R² = H, R³ = H
2h; R¹ = C₆H₁₁, R² = H, R³ = H
2i; R¹ = Ph, R² = C₂H₅, R³ = H
2j; R¹ = Ph, R² = H, R³ = 4-MeO
2k; R¹ = Ph, R² = H, R³ = 5-MeO
2l; R¹ = Ph, R² = H, R³ = 5-F
2m; R¹ = Ph, R² = H, R³ = 6-Cl
2n; R¹ = Ph, R² = H, R³ = 6-F₃C

In a nitrogen-filled glovebox, the appropriate 1-(1-arylvinyl)-1H-indole-2-carboxaldehyde (**1a-f**, **1i-n**) or 1-(1-alkylvinyl)-1H-indole-2-carboxaldehyde (**1g-h**) (0.10 mmol, 1.0 equiv), [Rh(COD)Cl]₂ (1.2 mg, 0.0025 mmol, 0.025 equiv), (S)-MeO-BIPHEP (2.9 mg, 0.0050 mmol, 0.050 equiv), AgBF₄ (1.0 mg, 0.0050 mmol, 0.050 equiv) and THF (0.7 mL) were added to a 1-dram vial. The vial was sealed with a PTFE/silicone-lined septum cap and removed from the glovebox. The reaction mixture was stirred at 60 °C in an oil bath for 16 h. The vial was removed from the oil bath and allowed to cool to room temperature. The reaction mixture was filtered through short plug of silica gel (eluting with 20 ml of 3:2 hexanes:EtOAc). The crude reaction mixture was concentrated under reduced pressure. The crude reaction mixture was purified by flash column silica gel chromatography (hexanes:EtOAc) to give the appropriate 3-

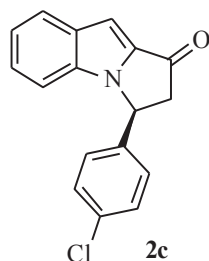
aryl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indol-1-ones (**2a-f**, **2i-n**) or 3-alkyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indol-1-ones (**2g-h**).



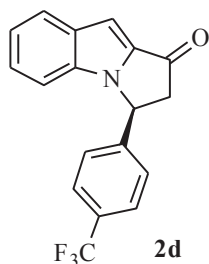
(S)-3-Phenyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indol-1-one (2a) (Table 2, entry 1): Prepared according to the general procedure from **1a** (25.0 mg, 0.101 mmol). The mixture was purified by flash column chromatography (90:10 hexane:EtOAc) to give **2a** as a light yellow solid in 92% yield (23.0 mg, 0.0930 mmol). The enantiomeric excess was determined by HPLC analysis (220 nm, 25 °C) t_R 15.6 min (major); t_R 12.9 min (minor) [Chiracel AD-H (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 95:5, 1.0 mL/min] to be 99% ee. $[\alpha]_D^{24} = -209.0^\circ$ (c 0.31, CHCl₃). **¹H NMR** (400 MHz, CDCl₃) δ 7.85 – 7.73 (m, 1H), 7.39 – 7.31 (m, 3H), 7.22 – 7.09 (m, 5H), 6.97 – 6.91 (m, 1H), 5.74 (dd, $J = 8.0, 4.0$ Hz, 1H), 3.68 (dd, $J = 18.4, 8.0$ Hz, 1H), 3.07 (dd, $J = 18.4, 4.0$ Hz, 1H). **¹³C NMR** (101 MHz, CDCl₃) δ 192.4, 140.2, 136.5, 135.2, 132.8, 129.6, 128.8, 126.3, 125.6, 124.5, 121.9, 112.0, 99.5, 57.5, 50.6. **HRMS** (EI): Calcd. for C₁₇H₁₃NO ([M]⁺): 247.0997, Found: 247.0989.



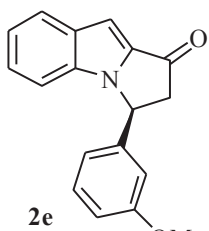
(S)-3-(4-Methoxyphenyl)-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indol-1-one (2b) (Table 2, entry 2): Prepared according to the general procedure from **1b** (28.0 mg, 0.101 mmol). The mixture was purified by flash column chromatography (90:10 hexane:EtOAc) to give **2b** as a light yellow solid in 99% yield (27.9 mg, 0.101 mmol). The enantiomeric excess was determined by HPLC analysis (220 nm, 25 °C) t_R 16.9 min (major); t_R 7.37 min (minor) [Chiracel OD-H (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 90:10, 1.0 mL/min] to be 99% ee. $[\alpha]_D^{24} = -226.0^\circ$ (c 0.88, CHCl₃). **¹H NMR** (400 MHz, CDCl₃) δ 7.81 – 7.72 (m, 1H), 7.16 (ddd, $J = 9.3, 7.8, 1.2$ Hz, 2H), 7.11 – 7.04 (m, 3H), 6.97 – 6.92 (m, 1H), 6.91 – 6.84 (m, 2H), 5.69 (dd, $J = 8.0, 4.0$ Hz, 1H), 3.80 (s, 3H), 3.65 (dd, $J = 18.4, 8.0$ Hz, 1H), 3.05 (dd, $J = 18.4, 4.0$ Hz, 1H). **¹³C NMR** (101 MHz, CDCl₃) δ 192.6, 159.9, 136.5, 135.2, 132.8, 132.2, 127.6, 125.5, 124.4, 121.8, 114.9, 112.1, 99.3, 57.1, 55.6, 50.7. **HRMS** (EI): Calcd. for C₁₈H₁₅NO₂ ([M]⁺): 277.1103, Found: 277.1109.



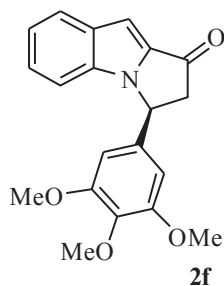
(S)-3-(4-Chlorophenyl)-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indol-1-one (2c) (Table 2, entry 3): Prepared according to the general procedure from **1c** (29.0 mg, 0.103 mmol). The mixture was purified by flash column chromatography (90:10 hexane:EtOAc) to give **2c** as a light yellow solid in 68% yield (19.7 mg, 0.070 mmol). The enantiomeric excess was determined by HPLC analysis (220 nm, 25 °C) t_R 28.9 min (major); t_R 33.5 min (minor) [Chiracel AD-H (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 95:5, 1.0 mL/min] to be 98% ee. $[\alpha]_D^{24} = +150.2^\circ$ (c 0.35, CHCl₃). **¹H NMR** (400 MHz, CDCl₃) δ 7.81 – 7.76 (m, 1H), 7.37 – 7.30 (m, 2H), 7.24 – 7.13 (m, 2H), 7.11 (d, $J = 0.4$ Hz, 1H), 7.10 – 7.03 (m, 2H), 6.92 (dq, $J = 8.4, 2.0, 1.2$ Hz, 1H), 5.74 (dd, $J = 8.0, 3.6$ Hz, 1H), 3.69 (dd, $J = 18.4, 8.0$ Hz, 1H), 3.02 (dd, $J = 18.4, 3.6$ Hz, 1H). **¹³C NMR** (101 MHz, CDCl₃) δ 191.9, 138.8, 136.4, 135.1, 134.8, 132.9, 129.9, 127.7, 125.8, 124.7, 122.1, 111.9, 99.9, 56.8, 50.5. **HRMS** (EI): Calcd. for C₁₇H₁₂ClNO ([M]⁺): 281.0607, Found: 281.0602.



(S)-3-(4-(Trifluoromethyl)phenyl)-2,3-dihydro-1H-pyrrolo[1,2-a]indol-1-one (2d) (Table 2, entry 4): Prepared according to a modified version of the general procedure from **1d** (32.0 mg, 0.101 mmol). In a nitrogen-filled glovebox, **1d** (32.0 mg, 0.101 mmol), [Rh(COD)Cl]₂ (2.5 mg, 0.00505 mmol, 0.0500 equiv), (*S*)-MeO-BIPHEP (5.9 mg, 0.0101 mmol, 0.100 equiv), AgBF₄ (2.0 mg, 0.0101 mmol, 0.100 equiv) and THF (0.7 mL) were added to a 1-dram vial. The vial was sealed with a PTFE/silicone-lined septum cap and removed from the glovebox. The reaction mixture was stirred at 60 °C in an oil bath for 16 h. The vial was removed from the oil bath and allowed to cool to room temperature. The reaction mixture was filtered through short plug of silica gel (eluting with 20 mol of 3:2 hexanes:EtOAc). The crude reaction mixture was concentrated under reduced pressure. The crude reaction mixture was purified by flash column silica gel chromatography (90:10 hexanes:EtOAc) to give **2d** as a light yellow solid in 70% yield (22.5 mg, 0.0713 mmol). The enantiomeric excess was determined by HPLC analysis (220 nm, 25 °C) *t*_R 34.6 min (major); *t*_R 47.9 min (minor) [Chiracel AD-H (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 99:1, 1.0 mL/min] to be 99% ee. [α]_D²⁴ = -253.0° (c 0.24, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.87 – 7.74 (m, 1H), 7.69 – 7.57 (m, 2H), 7.27 – 7.15 (m, 4H), 7.14 (d, *J* = 0.8 Hz, 1H), 6.91 (dq, *J* = 8.4, 2.4, 1.2 Hz, 1H), 5.83 (dd, *J* = 8.0, 3.6 Hz, 1H), 3.73 (dd, *J* = 18.4, 8.0 Hz, 1H), 3.03 (dd, *J* = 18.4, 3.6 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 191.5, 144.3, 136.4, 135.1, 132.9, 131.4, 131.0, 126.8, 126.8, 126.7, 126.7, 126.0, 125.5, 124.7, 122.8, 122.2, 111.8, 100.1, 56.9, 50.3. ¹⁹F NMR (CDCl₃, 376 MHz): δ -63.1. HRMS (EI): Calcd. for C₁₈H₁₂F₃NO ([M]⁺): 315.0871, Found: 315.0886.

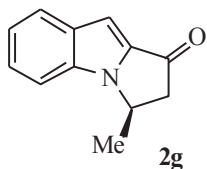


(S)-3-(3-Methoxyphenyl)-2,3-dihydro-1H-pyrrolo[1,2-a]indol-1-one (2e) (Table 2, entry 5): Prepared according to the general procedure from **1e** (28.0 mg, 0.101 mmol). The mixture was purified by flash column chromatography (90:10 hexane:EtOAc) to give **2e** as a light yellow solid in 92% yield (25.8 mg, 0.0930 mmol). The enantiomeric excess was determined by HPLC analysis (220 nm, 25 °C) *t*_R 14.5 min (major); *t*_R 10.5 min (minor) [Chiracel AD-H (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 90:10, 1.0 mL/min] to be 98% ee. [α]_D²³ = -206.6° (c 0.54, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.79 – 7.75 (m, 1H), 7.21 – 7.11 (m, 2H), 7.11 – 7.05 (m, 3H), 6.95 (dq, *J* = 8.4, 2.4, 1.2 Hz, 1H), 6.91 – 6.84 (m, 2H), 5.69 (dd, *J* = 8.0, 4.0 Hz, 1H), 3.80 (s, 3H), 3.65 (dd, *J* = 18.4, 8.0 Hz, 1H), 3.05 (dd, *J* = 18.4, 4.0 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 192.4, 160.6, 141.9, 136.5, 135.3, 132.8, 130.8, 125.6, 124.5, 121.9, 118.5, 113.9, 112.2, 99.5, 57.4, 55.6, 50.5. HRMS (EI): Calcd. for C₁₈H₁₅NO₂ ([M]⁺): 277.1103, Found: 277.1102.

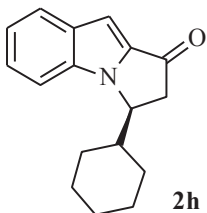


(S)-3-(3,4,5-Trimethoxyphenyl)-2,3-dihydro-1H-pyrrolo[1,2-a]indol-1-one (2f) (Table 2, entry 6): Prepared according to the general procedure from **1f** (34.0 mg, 0.100 mmol). The mixture was purified by flash column chromatography (80:20 hexane:EtOAc) to give **2f** as a light yellow solid in 82% yield (27.8 mg, 0.0820 mmol). The enantiomeric excess was determined by HPLC analysis (220 nm, 25 °C) *t*_R 21.8 min (major); *t*_R 18.8 min (minor) [Chiracel AD-H (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 90:10, 1.0 mL/min] to be 99% ee. [α]_D²⁴ = -229.1° (c 0.48, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.80 – 7.76 (m, 1H), 7.20 (dddd, *J* =

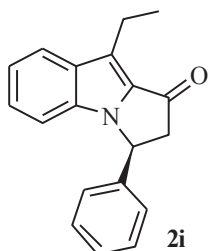
24.4, 14.8, 6.8, 0.8 Hz, 2H), 7.10 (d, $J = 0.4$ Hz, 1H), 7.01 (dq, $J = 8.4, 2.0, 1.2$ Hz, 1H), 6.32 (s, 2H), 5.66 (dd, $J = 8.0, 3.6$ Hz, 1H), 3.84 (s, 3H), 3.74 (s, 6H), 3.66 (dd, $J = 18.4, 8.0$ Hz, 1H), 3.08 (dd, $J = 18.4, 3.6$ Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 192.4, 154.3, 138.3, 136.6, 135.9, 135.4, 132.8, 125.7, 124.5, 122.0, 103.2, 99.7, 61.2, 57.8, 56.5, 50.6. HRMS (EI): Calcd. for $\text{C}_{20}\text{H}_{19}\text{NO}_4$ ($[\text{M}]^+$): 337.1314, Found: 337.1306.



(R)-3-Methyl-2,3-dihydro-1H-pyrrolo[1,2-a]indol-1-one (2g) (Table 2, entry 7): Prepared according to the general procedure from **1g** (19.0 mg, 0.102 mmol). The mixture was purified by flash column chromatography (80:20 hexane:EtOAc) to give **2g** as a light yellow solid in 99% yield (18.9 mg, 0.102 mmol). The enantiomeric excess was determined by HPLC analysis (220 nm, 25 °C) t_R 27.2 min (major); t_R 23.9 min (minor) [Chiracel AD-H (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 99:1, 1.0 mL/min] to be 99% ee. $[\alpha]_D^{24} = -127.6^\circ$ (c 0.75, CHCl_3). ^1H NMR (400 MHz, CDCl_3) δ 7.77 (d, $J = 8.4$, 1H), 7.53 – 7.43 (m, 1H), 7.37 (t, $J = 7.6$ Hz, 1H), 7.19 (t, $J = 7.6$ Hz, 1H), 6.99 (bs, 1H), 4.99 – 4.83 (m, 1H), 3.43 (dd, $J = 18.4, 7.6$ Hz, 1H), 2.80 (dd, $J = 18.4, 3.2$ Hz, 1H), 1.69 (d, $J = 6.4$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 193.1, 135.9, 134.9, 132.7, 125.4, 124.7, 121.6, 111.5, 110.3, 99.1, 49.6, 48.7, 22.0. HRMS (EI): Calcd. for $\text{C}_{12}\text{H}_{11}\text{NO}$ ($[\text{M}]^+$): 185.0841, Found: 185.0842.

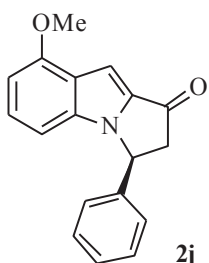


(S)-3-Cyclohexyl-2,3-dihydro-1H-pyrrolo[1,2-a]indol-1-one (2h) (Table 2, entry 8): Prepared according to a modified version of the general procedure from **1h** (26.0 mg, 0.102 mmol). In a nitrogen-filled glovebox, **1h** (26.0 mg, 0.102 mmol), $[\text{Rh}(\text{COD})\text{Cl}]_2$ (1.3 mg, 0.00255 mmol, 0.0250 equiv), (*S*)-MeO-BIPHEP (3.0 mg, 0.00513 mmol, 0.0500 equiv), AgBF_4 (1.0 mg, 0.00513 mmol, 0.0500 equiv) and 1,4-dioxane (0.7 mL) were added to a 1-dram vial. The vial was sealed with a PTFE/silicone-lined septum cap and removed from the glovebox. The reaction mixture was stirred at 101 °C in an oil bath for 16 h. The vial was removed from the oil bath and allowed to cool to room temperature. The reaction mixture was filtered through short plug of silica gel (eluting with 20 mol of 3:2 hexanes:EtOAc). The crude reaction mixture was concentrated under reduced pressure. The crude reaction mixture was purified by flash column silica gel chromatography (90:10 hexanes:EtOAc) to give **2h** as a light yellow solid in 45% yield (11.7 mg, 0.0462 mmol). The enantiomeric excess was determined by HPLC analysis (220 nm, 25 °C) t_R 12.3 min (major); t_R 8.66 min (minor) [Chiracel AD-H (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 95:5, 1.0 mL/min] to be 95% ee. $[\alpha]_D^{24} = +453.9^\circ$ (c 0.16, CHCl_3). ^1H NMR (400 MHz, CDCl_3) δ 7.77 (d, $J = 8.0$ Hz, 1H), 7.54 – 7.45 (m, 1H), 7.35 (t, $J = 7.6$ Hz, 1H), 7.18 (t, $J = 7.6$ Hz, 1H), 6.97 (bs, 1H), 4.86 – 4.77 (m, 1H), 3.14 (dd, $J = 18.4, 8.0$ Hz, 1H), 2.96 (dd, $J = 18.4, 2.4$ Hz, 1H), 2.37 – 2.25 (m, 1H), 1.89 – 1.76 (m, 2H), 1.74 – 1.55 (m, 2H), 1.41 – 1.19 (m, 2H), 1.19 – 0.78 (m, 4H). ^{13}C NMR (101 MHz, CDCl_3) δ 193.5, 136.5, 135.2, 132.7, 125.3, 124.7, 121.6, 111.9, 98.7, 58.4, 42.5, 41.4, 30.0, 26.5, 25.8, 25.0. HRMS (EI): Calcd. for $\text{C}_{17}\text{H}_{19}\text{NO}$ ($[\text{M}]^+$): 253.1467, Found: 253.1468.



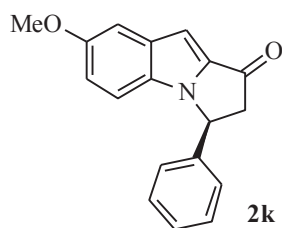
(S)-9-Ethyl-3-phenyl-2,3-dihydro-1H-pyrrolo[1,2-a]indol-1-one (2i)

(Table 3, entry 1): Prepared according to the general procedure from **1i** (28.0 mg, 0.101 mmol). The mixture was purified by flash column chromatography (90:10 hexane:EtOAc) to give **2i** as a light yellow solid in 89% yield (25.0 mg, 0.0900 mmol). The enantiomeric excess was determined by HPLC analysis (220 nm, 25 °C) t_R 8.57 min (major); t_R 12.6 min (minor) [Chiracel OD-H (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 95:5, 1.0 mL/min] to be 98% ee. $[\alpha]_D^{24} = -160.9^\circ$ (c 0.65, CHCl₃). **¹H NMR** (400 MHz, CDCl₃) δ 7.78 (dq, J = 8.0, 1.2, 0.4 Hz, 1H), 7.40 – 7.29 (m, 3H), 7.21 – 7.08 (m, 4H), 6.88 (dt, J = 8.4, 0.8 Hz, 1H), 5.68 (dd, J = 8.0, 4.0 Hz, 1H), 3.65 (dd, J = 18.4, 8.0 Hz, 1H), 3.12 (qd, J = 15.2, 7.6, 1.6 Hz, 2H), 3.04 (dd, J = 18.4, 4.0 Hz, 1H), 1.40 (t, J = 7.2 Hz, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 192.6, 140.7, 135.0, 132.8, 132.1, 129.6, 128.7, 126.4, 125.6, 122.7, 120.9, 119.9, 112.0, 57.1, 51.1, 17.9, 15.9. **HRMS** (EI): Calcd. for C₁₉H₁₇NO ([M]⁺): 275.1310, Found: 275.1315.



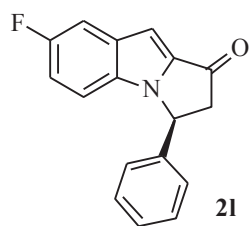
(S)-8-Methoxy-3-phenyl-2,3-dihydro-1H-pyrrolo[1,2-a]indol-1-one (2j)

(Table 3, entry 2): Prepared according to the general procedure from **1j** (28.0 mg, 0.100 mmol). The mixture was purified by flash column chromatography (90:10 hexane:EtOAc) to give **2j** as a light yellow solid in 90% yield (25.2 mg, 0.0900 mmol). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 20.4 min (major); t_R 27.8 min (minor) [Chiracel AD-H (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 95:5, 1.0 mL/min] to be 99% ee. $[\alpha]_D^{24} = -185.3^\circ$ (c 0.71, CHCl₃). **¹H NMR** (400 MHz, CDCl₃) δ 7.38 – 7.31 (m, 2H), 7.22 (d, J = 0.4 Hz, 1H), 7.14 – 7.09 (m, 3H), 6.50 (dd, J = 11.6, 8.4 Hz, 2H), 5.71 (dd, J = 8.0, 4.0 Hz, 1H), 3.96 (s, 3H), 3.67 (dd, J = 18.4, 8.0 Hz, 1H), 3.05 (dd, J = 18.4, 4.0 Hz, 1H). **¹³C NMR** (101 MHz, CDCl₃) δ 191.9, 155.9, 140.3, 136.5, 135.4, 129.6, 128.8, 126.7, 126.3, 124.5, 104.8, 100.4, 97.4, 57.5, 55.7, 50.7. **HRMS** (EI): Calcd. for C₁₈H₁₅NO₂ ([M]⁺): 277.1103, Found: 277.1107.



(S)-7-Methoxy-3-phenyl-2,3-dihydro-1H-pyrrolo[1,2-a]indol-1-one (2k)

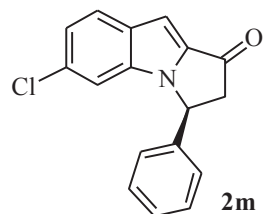
(Table 3, entry 3): Prepared according to the general procedure from **1k** (28.0 mg, 0.101 mmol). The mixture was purified by flash column chromatography (90:10 hexane:EtOAc) to give **2k** as a light yellow solid in 97% yield (27.2 mg, 0.0980 mmol). The enantiomeric excess was determined by HPLC analysis (220 nm, 25 °C) t_R 23.7 min (major); t_R 17.8 min (minor) [Chiracel AD-H (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 95:5, 1.0 mL/min] to be 98% ee. $[\alpha]_D^{24} = -226.2^\circ$ (c 0.88, CHCl₃). **¹H NMR** (400 MHz, CDCl₃) δ 7.39 – 7.30 (m, 3H), 7.15 – 7.09 (m, 3H), 7.01 (d, J = 0.4 Hz, 1H), 6.89 – 6.79 (m, 2H), 5.72 (dd, J = 8.0, 4.0 Hz, 1H), 3.83 (s, 3H), 3.67 (dd, J = 18.8, 8.0 Hz, 1H), 3.05 (dd, J = 18.8, 4.0 Hz, 1H). **¹³C NMR** (101 MHz, CDCl₃) δ 191.9, 155.5, 140.3, 137.0, 133.3, 130.9, 129.6, 128.8, 126.3, 118.2, 113.0, 103.3, 98.9, 57.5, 55.8, 50.5. **HRMS** (EI): Calcd. for C₁₈H₁₅NO₂ ([M]⁺): 277.1103, Found: 277.1105.



(S)-7-Fluoro-3-phenyl-2,3-dihydro-1H-pyrrolo[1,2-a]indol-1-one (2l)

(Table 3, entry 4): Prepared according to the general procedure from **1l** (27.0 mg, 0.102 mmol). The mixture was purified by flash column chromatography (90:10 hexane:EtOAc) to give **2l** as a light yellow solid in 92% yield (24.9 mg, 0.0940 mmol). The enantiomeric excess was determined by HPLC analysis (220 nm, 25 °C) t_R 16.9 min (major); t_R 12.4 min (minor) [Chiracel AD-H (0.46 cm x 25 cm)(from Daicel Chemical

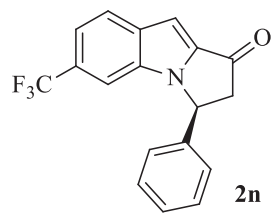
Ind., Ltd.) hexane/*i*-PrOH, 95:5, 1.0 mL/min] to be 98% ee. $[\alpha]_D^{24} = -145.6^\circ$ (c 0.73, CHCl₃). **¹H NMR** (400 MHz, CDCl₃) δ 7.43 – 7.31 (m, 4H), 7.17 – 7.08 (m, 2H), 7.04 (d, $J = 0.4$ Hz, 1H), 6.95 (td, $J = 9.2, 2.4$ Hz, 1H), 6.86 (dd, $J = 9.2, 4.4$ Hz, 1H), 5.73 (dd, $J = 8.0, 4.0$ Hz, 1H), 3.68 (dd, $J = 18.8, 8.0$ Hz, 1H), 3.06 (dd, $J = 18.8, 4.0$ Hz, 1H). **¹³C NMR** (101 MHz, CDCl₃) δ 192.0, 159.9, 157.5, 139.9, 137.9, 133.0, 132.9, 131.9, 129.7, 129.0, 126.3, 115.4, 115.1, 113.1, 113.0, 108.4, 108.2, 99.2, 57.7, 50.5. **¹⁹F NMR** (CDCl₃, 376 MHz): δ -121.3. **HRMS** (EI): Calcd. for C₁₇H₁₂FNO ([M]⁺): 265.0903, Found: 265.0899.



(S)-6-Chloro-3-phenyl-2,3-dihydro-1H-pyrrolo[1,2-a]indol-1-one

(2m) (Table 3, entry 5): Prepared according to the general procedure from **1m** (28.5 mg, 0.101 mmol). The mixture was purified by flash column chromatography (90:10 hexane:EtOAc) to give **2m** as a light yellow solid in 82% yield (23.4 mg, 0.0830 mmol). The enantiomeric excess was determined by HPLC analysis (220 nm, 25 °C) t_R 34.5 min (major); t_R 58.3 min (minor) [Chiracel AD-H (0.46 cm x 25 cm)(from

Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 99:1, 1.0 mL/min] to be 98% ee. $[\alpha]_D^{24} = -270.6^\circ$ (c 0.70, CHCl₃). **¹H NMR** (400 MHz, CDCl₃) δ 7.69 (d, $J = 8.8$, 1H), 7.44 – 7.30 (m, 3H), 7.15 – 7.08 (m, 3H), 7.06 (d, $J = 0.8$ Hz, 1H), 6.93 (bs, 1H), 5.71 (dd, $J = 8.0, 4.0$ Hz, 1H), 3.68 (dd, $J = 18.8, 8.0$ Hz, 1H), 3.06 (dd, $J = 18.8, 4.0$ Hz, 1H). **¹³C NMR** (101 MHz, CDCl₃) δ 191.6, 139.4, 136.9, 134.9, 131.3, 130.9, 129.5, 128.8, 125.9, 125.1, 122.7, 111.3, 99.4, 57.3, 50.2. **HRMS** (EI): Calcd. for C₁₇H₁₂ClNO ([M+H]⁺): 281.0607, Found: 281.0594.

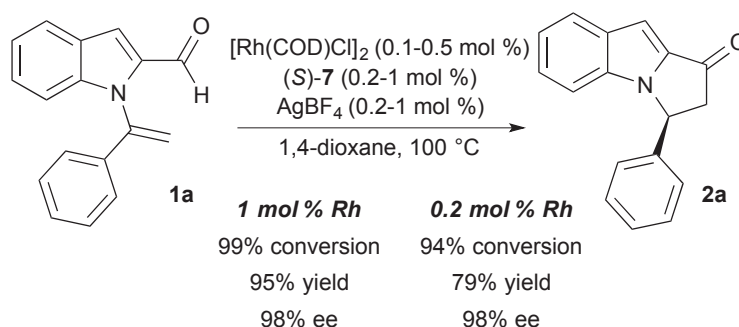


(S)-3-Phenyl-6-(trifluoromethyl)-2,3-dihydro-1H-pyrrolo[1,2-a]indol-1-one

(2n) (Table 3, entry 6): Prepared according to the general procedure from **1n** (32.0 mg, 0.101 mmol). The mixture was purified by flash column chromatography (90:10 hexane:EtOAc) to give **2n** as a light yellow solid in 81% yield (26.0 mg, 0.0820 mmol). The enantiomeric excess was determined by HPLC analysis (220 nm, 25 °C) t_R 29.9 min (major); t_R 45.6 min (minor) [Chiracel AD-H (0.46 cm x 25 cm)(from

Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 99:1, 1.0 mL/min] to be 99% ee. $[\alpha]_D^{24} = -234.1^\circ$ (c 0.73, CHCl₃). **¹H NMR** (400 MHz, CDCl₃) δ 7.88 (d, $J = 8.4$ Hz, 1H), 7.43 – 7.33 (m, 4H), 7.24 – 7.20 (m, 1H), 7.17 – 7.10 (m, 3H), 5.81 (dd, $J = 8.0, 4.0$ Hz, 1H), 3.72 (dd, $J = 18.8, 8.0$ Hz, 1H), 3.11 (dd, $J = 18.8, 4.0$ Hz, 1H). **¹³C NMR** (101 MHz, CDCl₃) δ 192.2, 139.5, 138.8, 134.6, 133.7, 129.9, 129.3, 127.4, 127.1, 126.2, 126.1, 125.2, 123.4, 118.2, 109.6, 99.3, 57.8, 50.5. **¹⁹F NMR** (CDCl₃, 376 MHz): δ -61.9. **HRMS** (EI): Calcd. for C₁₈H₁₂F₃NO ([M]⁺): 315.0871, Found: 315.0878.

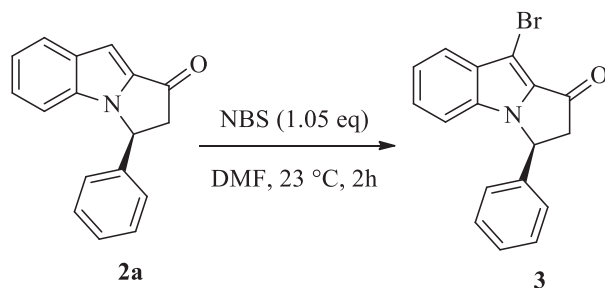
Procedures for Synthesis of **2a** at 0.2 and 1 mol % Catalyst Loading



1 mol % Catalyst Loading: In a nitrogen-filled glovebox, 1-(1-phenylvinyl)-1*H*-indole-2-carboxaldehyde (**1a**) (100 mg, 0.400 mmol, 1.00 equiv), [Rh(COD)Cl]₂ (1.0 mg, 0.0020 mmol, 0.0050 equiv), (*S*)-MeO-BIPHEP (**7**) (2.3 mg, 0.0040 mmol, 0.010 equiv), AgBF₄ (0.8 mg, 0.004 mmol, 0.01 equiv) and THF (2.8 mL) were added to a 1-dram vial. The vial was sealed with a PTFE/silicone-lined septum cap and removed from the glovebox. The reaction mixture was stirred at 101 °C in an oil bath for 16 h. The vial was removed from the oil bath and allowed to cool to room temperature. The reaction mixture was filtered through short plug of silica gel (eluting with 50 ml of 3:2 hexanes:EtOAc). The crude reaction mixture was concentrated under reduced pressure. The crude reaction mixture was purified by flash column silica gel chromatography (90:10 hexanes:EtOAc) to give (*S*)-3-phenyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indol-1-one (**2a**) as a light yellow solid in 95% yield (95 mg, 0.38 mmol). The enantiomeric excess was determined by HPLC analysis (220 nm, 25 °C) *t*_R 15.6 min (major); *t*_R 12.9 min (minor) [Chiracel AD-H (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 95:5, 1.0 mL/min] to be 98% ee.

0.2 mol % Catalyst Loading: In a nitrogen-filled glovebox, 1-(1-phenylvinyl)-1*H*-indole-2-carboxaldehyde (**1a**) (500 mg, 2.0 mmol, 1.0 equiv), [Rh(COD)Cl]₂ (1.0 mg, 0.0020 mmol, 0.0010 equiv), (*S*)-MeO-BIPHEP (**7**) (2.3 mg, 0.0040 mmol, 0.0020 equiv), AgBF₄ (0.8 mg, 0.0040 mmol, 0.0020 equiv) and THF (14 mL) were added to a 20 mL scintillation vial. The vial was sealed with a PTFE/silicone-lined septum cap and removed from the glovebox. The reaction mixture was stirred at 101 °C in an oil bath for 16 h. The vial was removed from the oil bath and allowed to cool to room temperature. The reaction mixture was filtered through short plug of silica gel (eluting with 150 ml of 3:2 hexanes:EtOAc). The crude reaction mixture was concentrated under reduced pressure. The crude reaction mixture was purified by flash column silica gel chromatography (90:10 hexanes:EtOAc) to give (*S*)-3-phenyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indol-1-one (**2a**) as a light yellow solid in 79% yield (395 mg, 1.60 mmol). The enantiomeric excess was determined by HPLC analysis (220 nm, 25 °C) *t*_R 15.6 min (major); *t*_R 12.9 min (minor) [Chiracel AD-H (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 95:5, 1.0 mL/min] to be 98% ee.

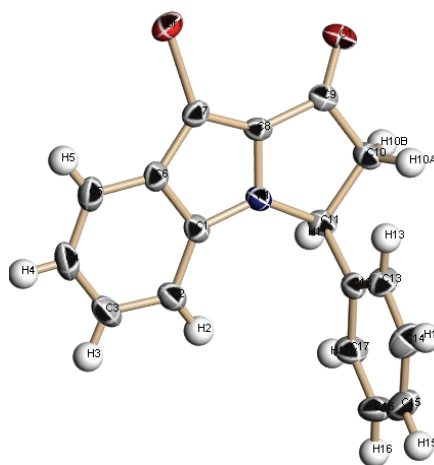
Synthesis of (*S*)-9-Bromo-3-phenyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indol-1-one (**3**)

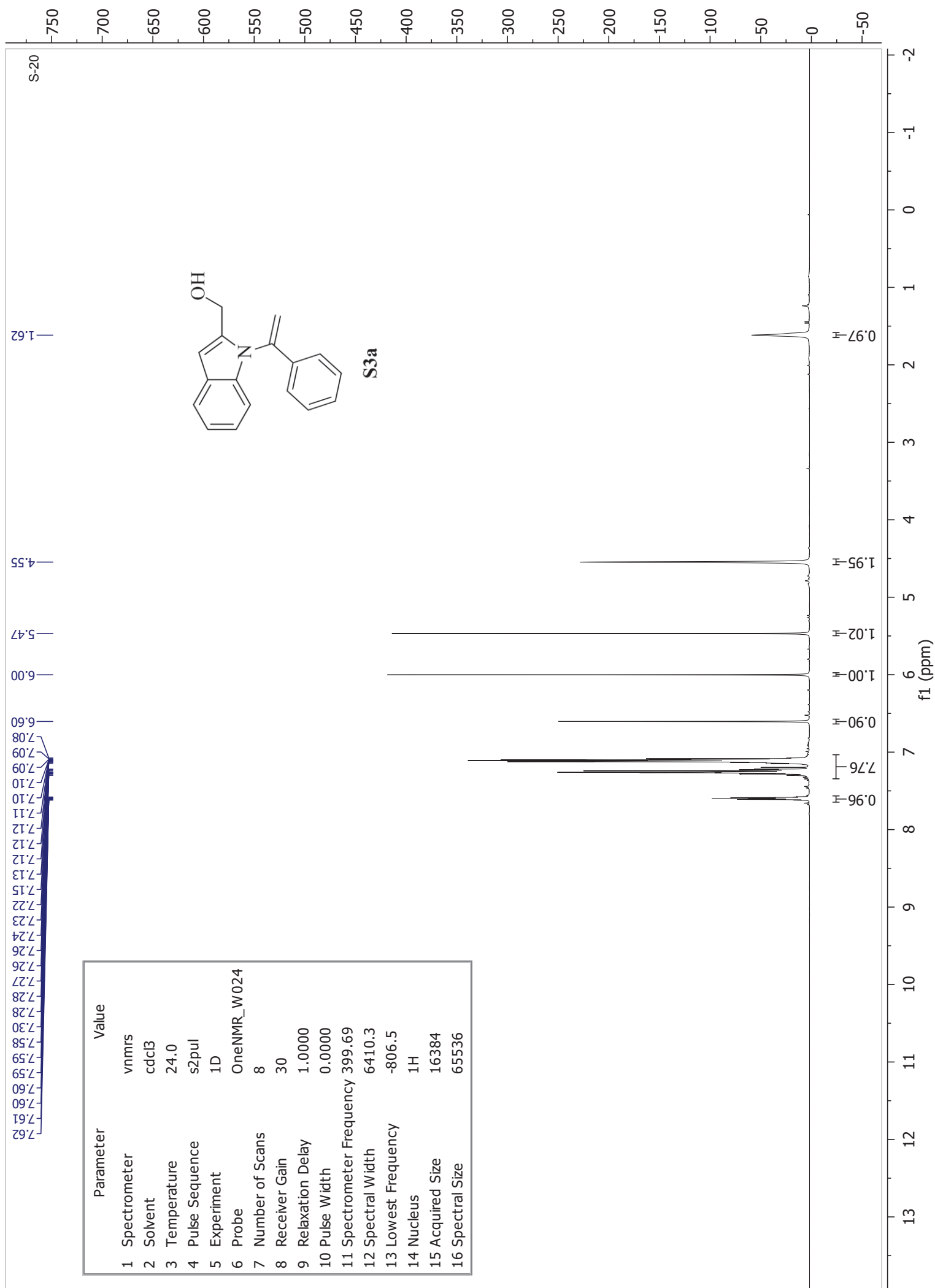


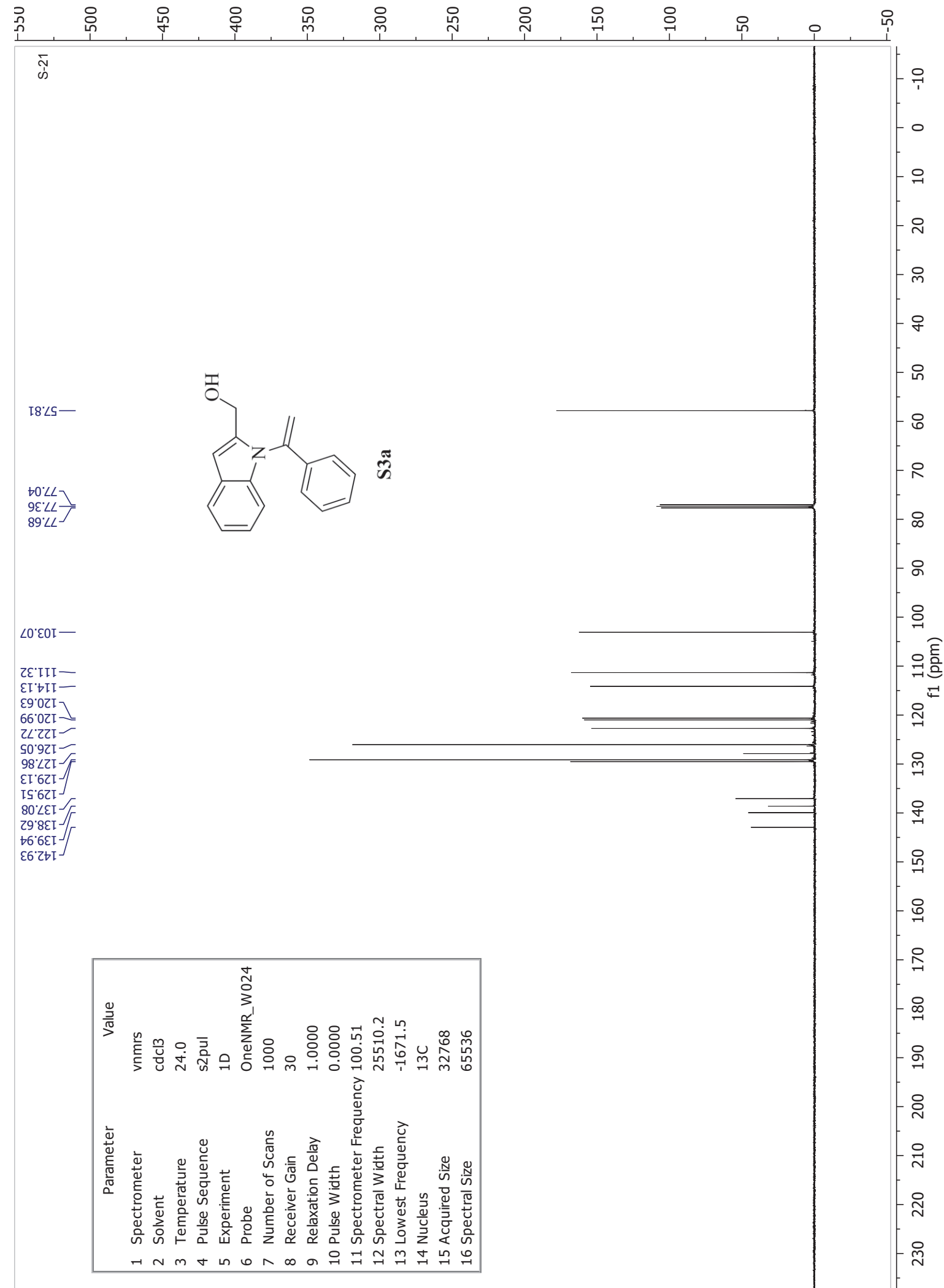
To a solution of (*S*)-3-phenyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indol-1-one (**2a**) (150.0 mg, 0.606 mmol) in DMF (10 ml) was added *N*-bromosuccinimide (113.0 mg, 0.637 mmol). The reaction mixture was stirred for 2 hours at 23 °C under a nitrogen atmosphere. The reaction mixture was diluted with ethyl acetate and washed with brine. The organic layer was dried over magnesium sulfate, filtered, and concentrated under reduced pressure. The crude product was purified by flash column silica gel chromatography (90:10 hexane:EtOAc) to give (*S*)-9-bromo-3-phenyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indol-1-one (**3**) as an off-white solid in 88% yield (175 mg, 0.535 mmol). The resulting product was recrystallized from methanol to obtain colorless single crystals for single crystal XRD analysis. m.p. = 134-136 °C (decomposition) $[\alpha]_D^{24} = -151.2^\circ$ (c 0.65, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.77 – 7.68 (m, 1H), 7.46 – 7.30 (m, 3H), 7.25 – 7.19 (m, 2H), 7.18 – 7.12 (m, 2H), 6.96 – 6.86 (m, 1H), 5.71 (dd, *J* = 8.0, 4.0 Hz, 1H), 3.70 (dd, *J* = 18.8, 8.0 Hz, 1H), 3.10 (dd, *J* = 18.4, 4.0 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 190.6, 139.7, 134.9, 132.9, 132.2, 129.7, 129.1, 126.7, 126.4, 122.6, 112.2, 88.8, 57.6, 50.9. HRMS (EI): Calcd. for C₁₇H₁₂BrNO ([M]⁺): 325.0102, Found: 325.0108.

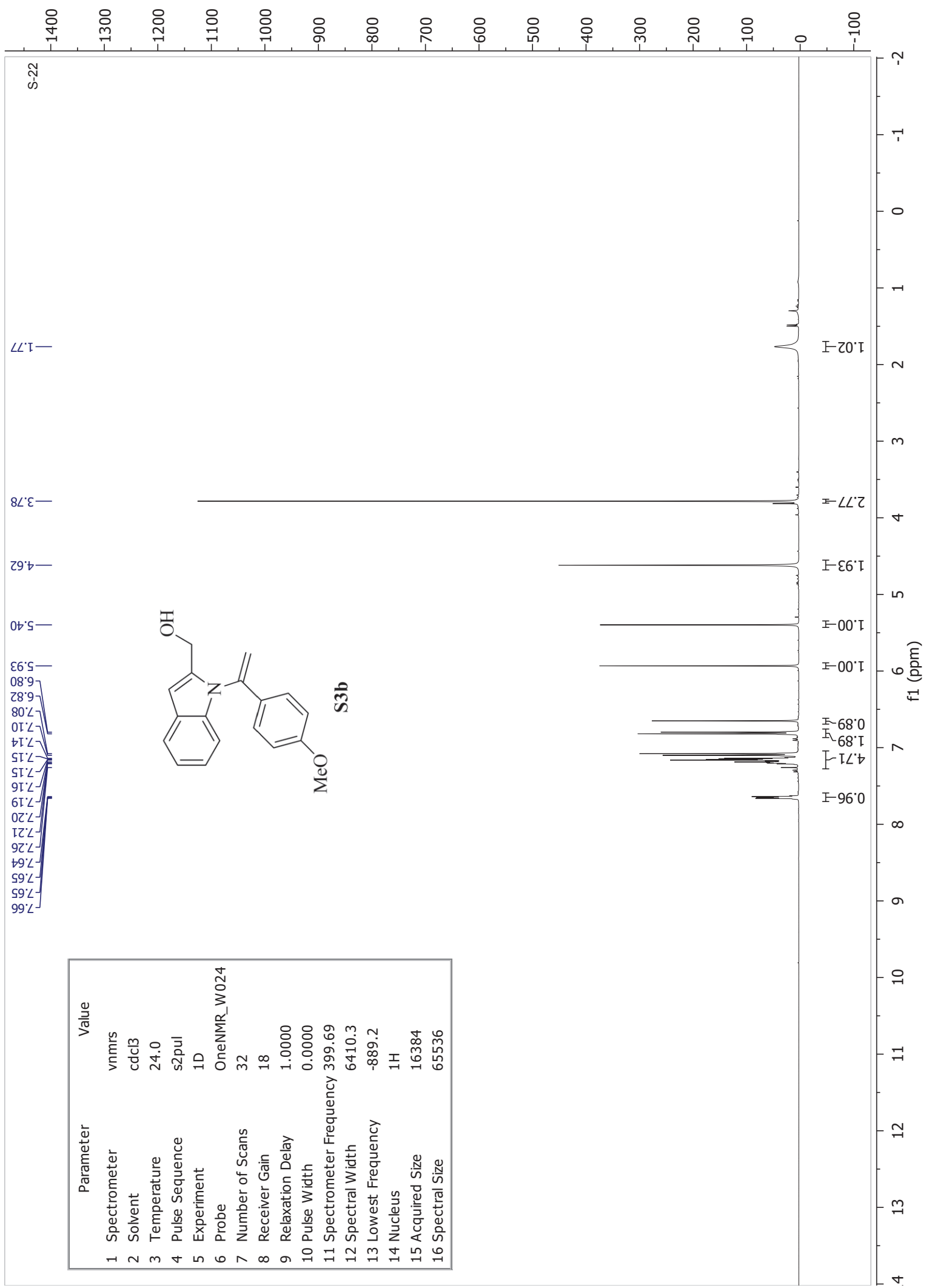
Absolute Stereochemistry and Structure of **3**

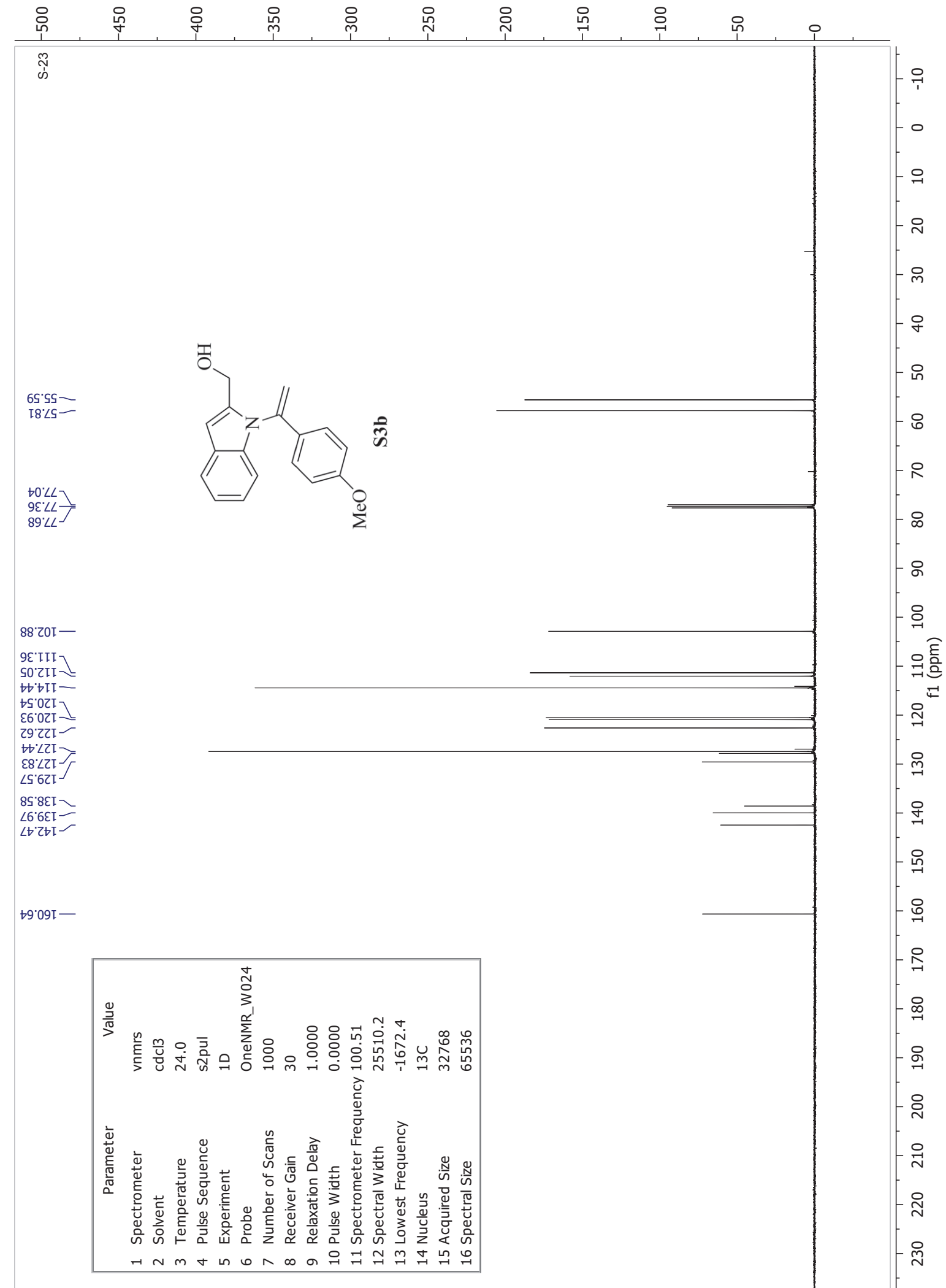
Supplementary X-ray diffraction data and structure refinement for **3** is contained in CCDC 976167. These data can be accessed free of charge from the Cambridge Crystallographic Data Center at www.ccdc.cam.ac.uk/data_request/cif.

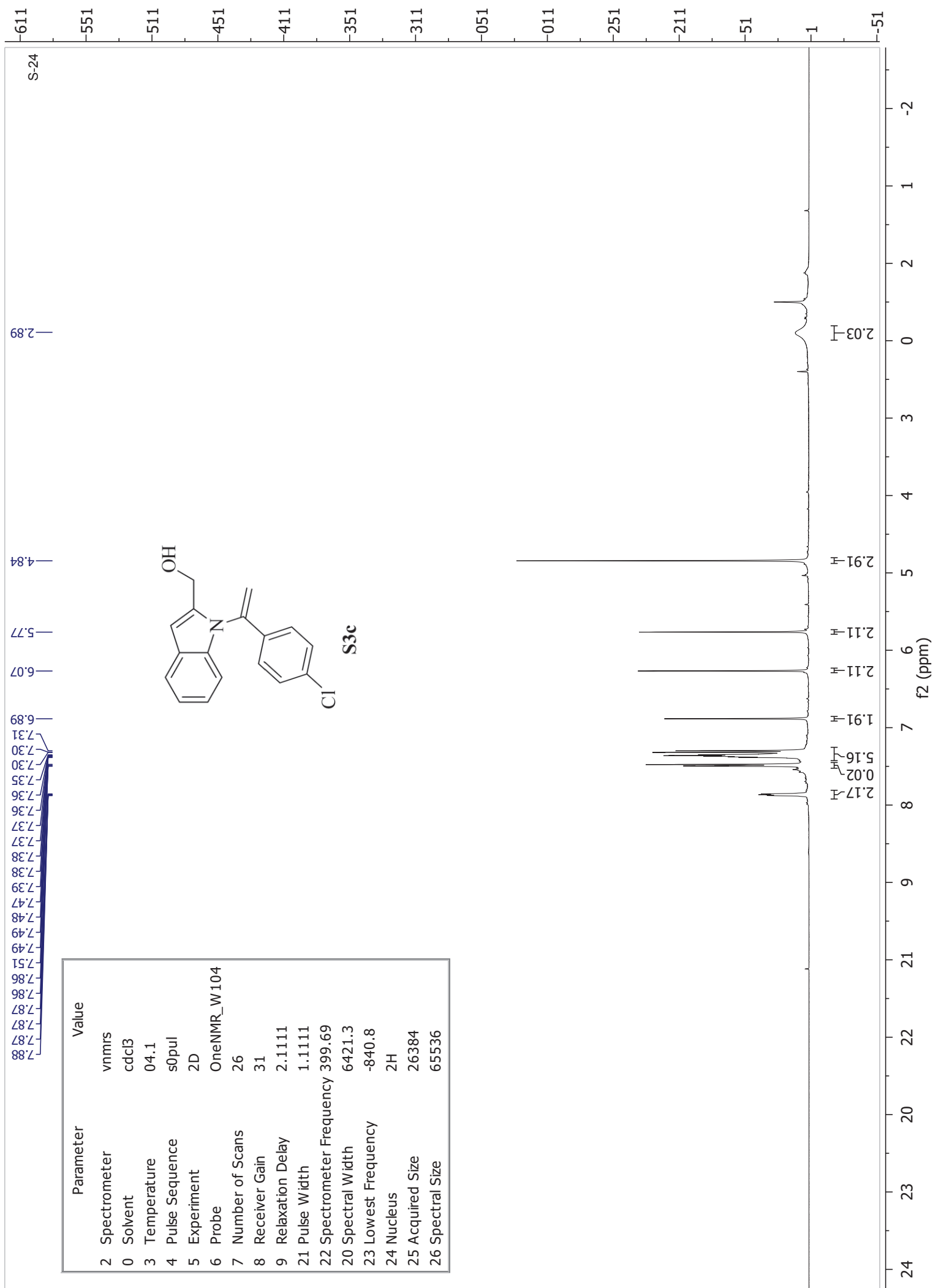




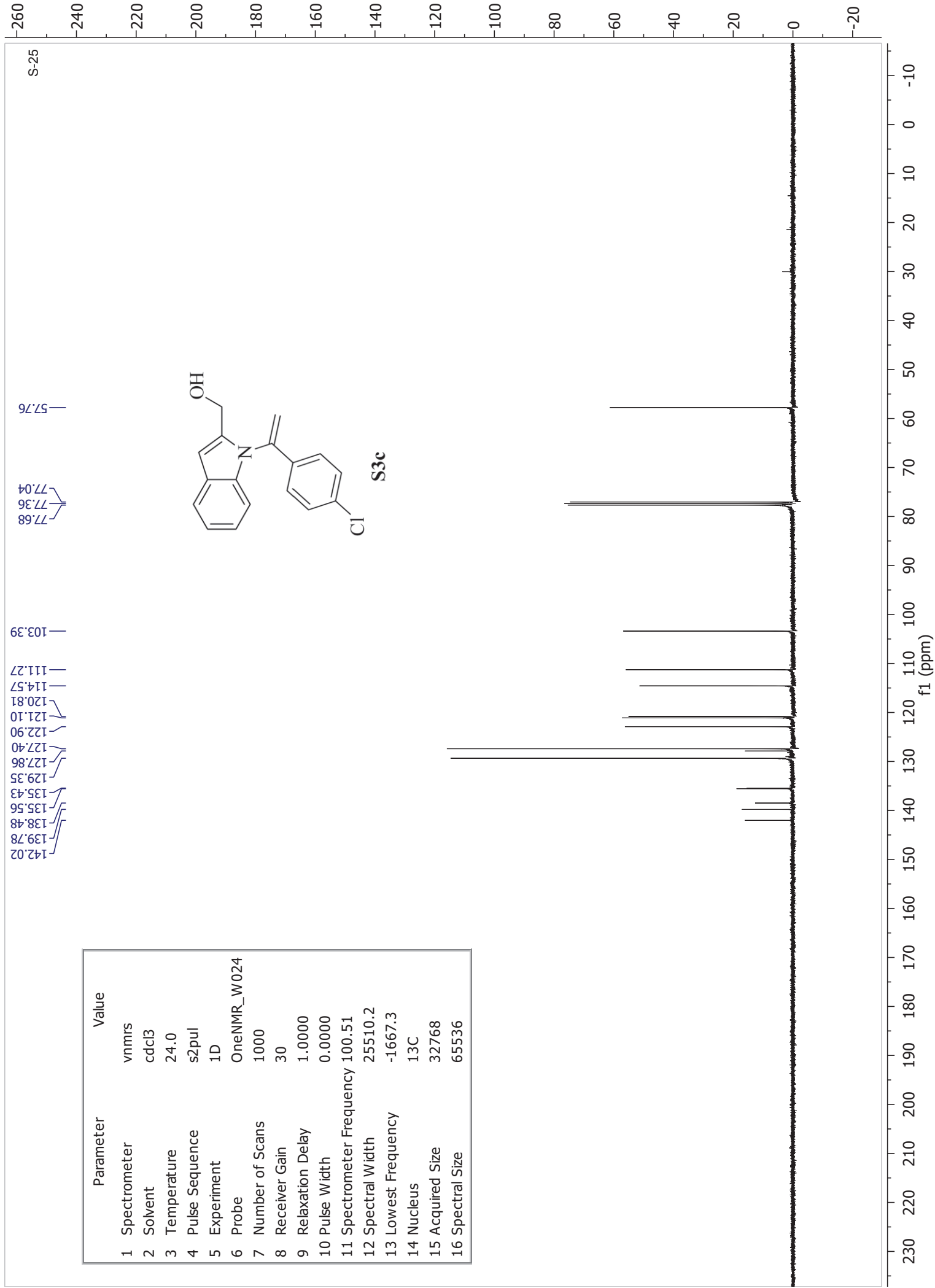


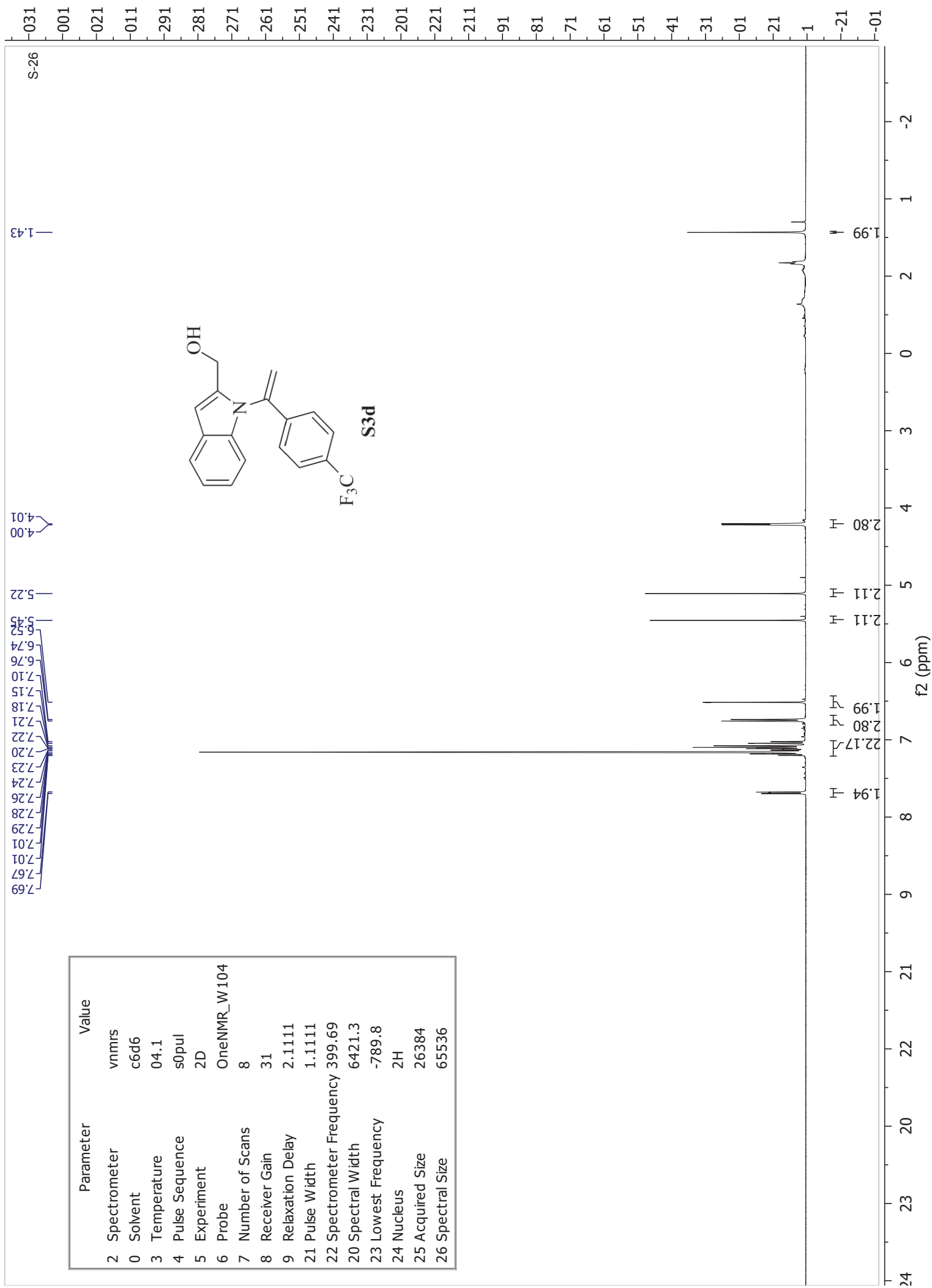


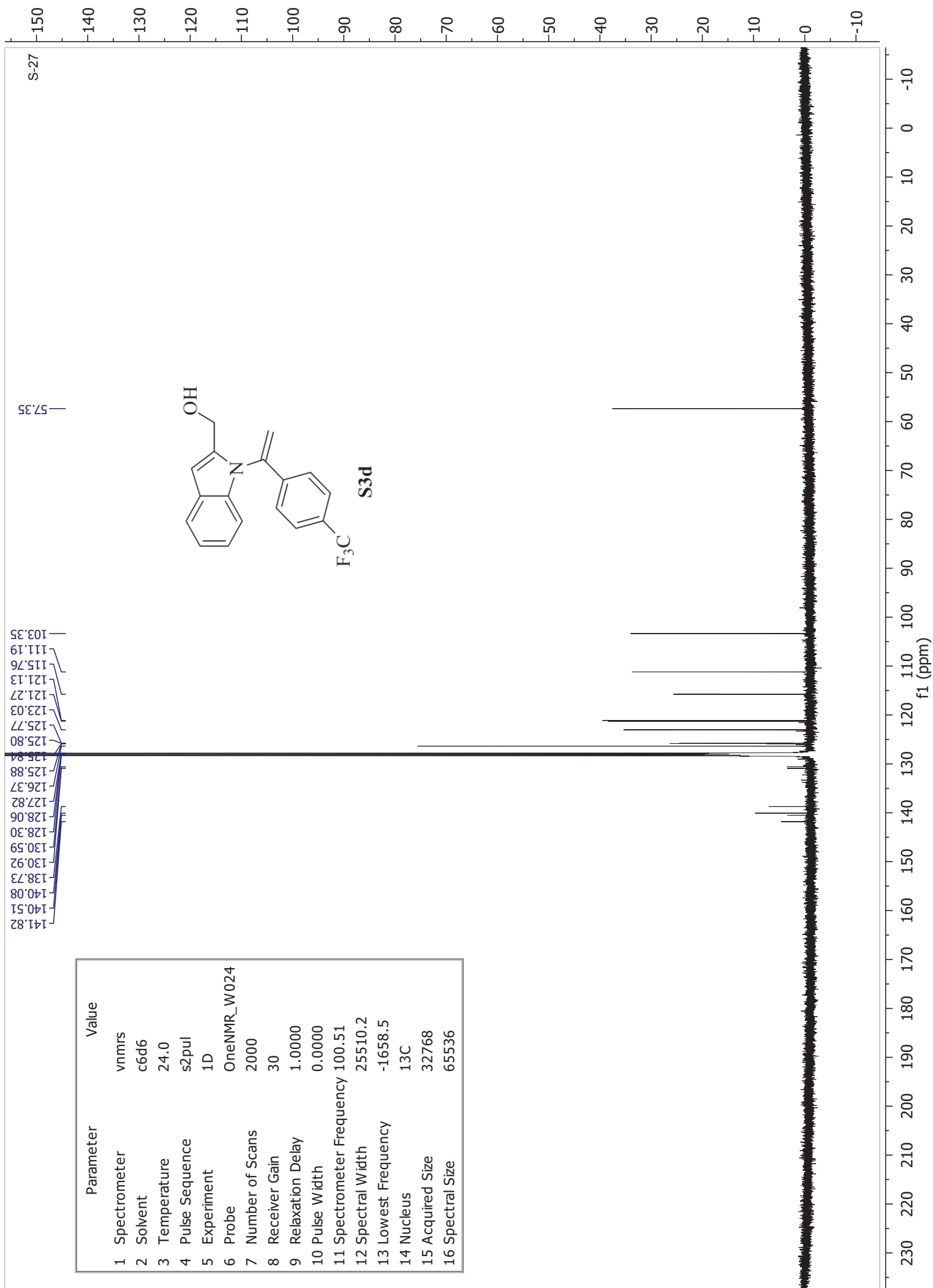


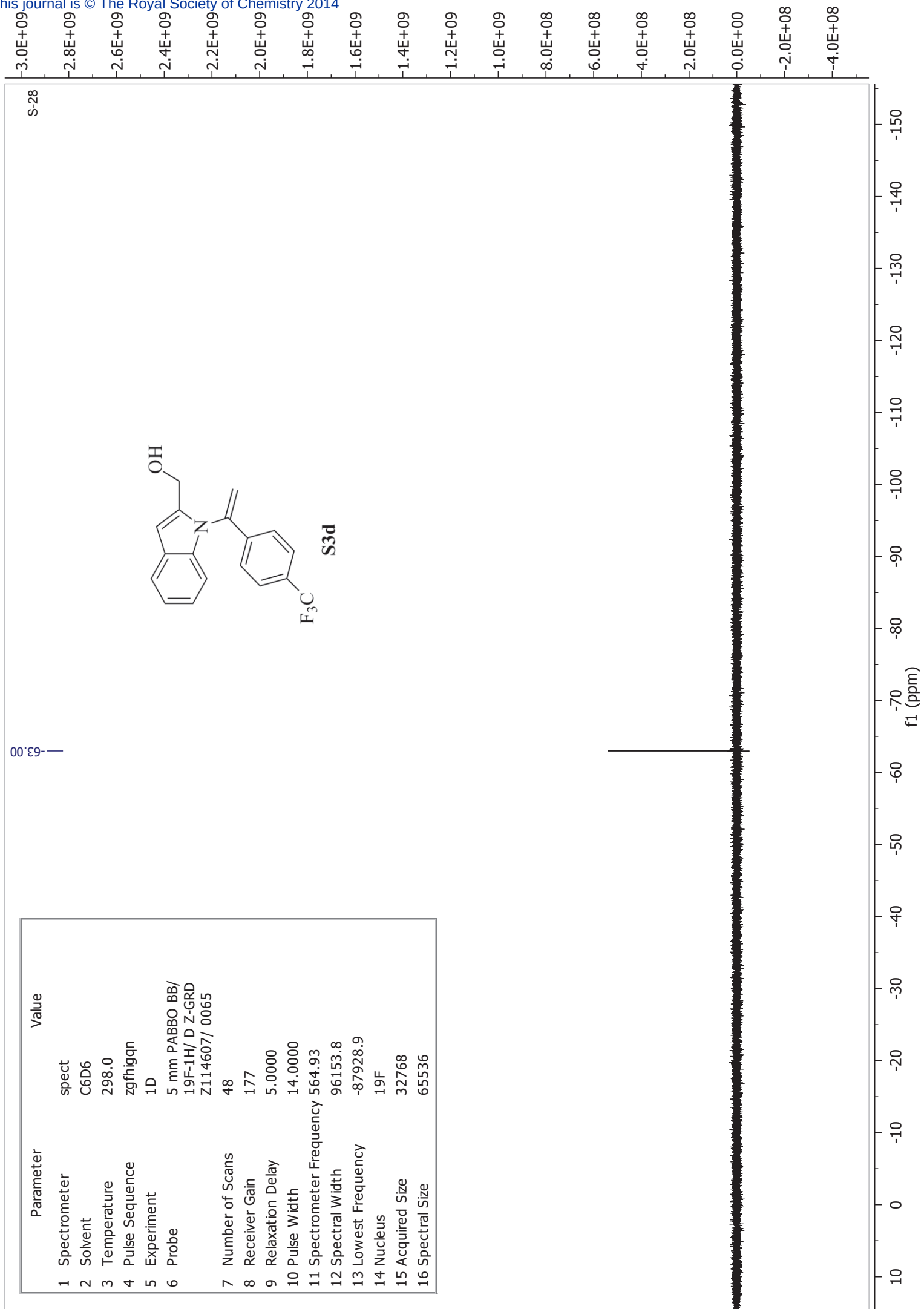


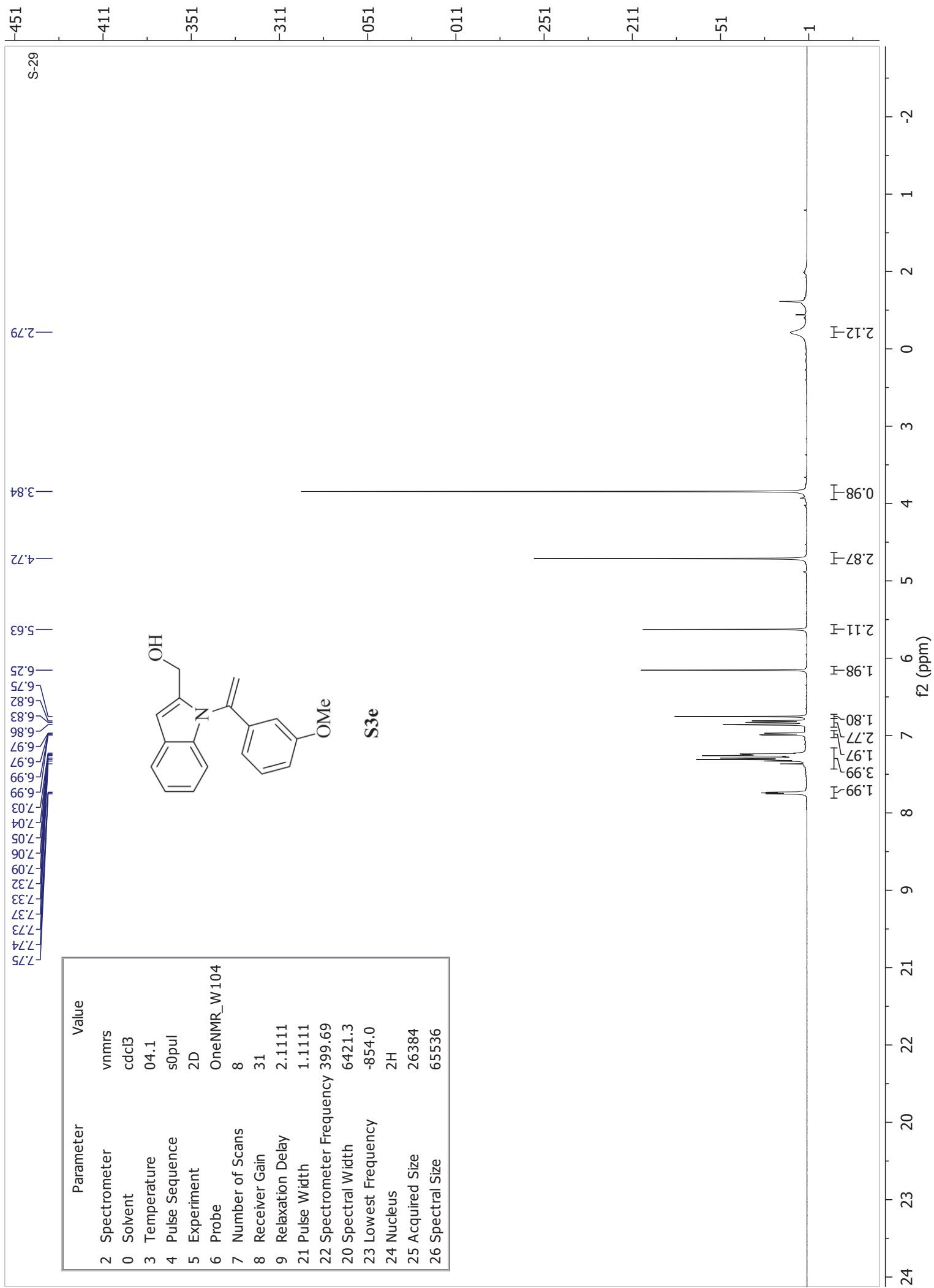
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5 Experiment	1D
6 Probe	OneNMR_W024
7 Number of Scans	1000
8 Receiver Gain	30
9 Relaxation Delay	1.0000
10 Pulse Width	0.0000
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13 Lowest Frequency	-1667.3
14 Nucleus	¹³ C
15 Acquired Size	32768
16 Spectral Size	65536

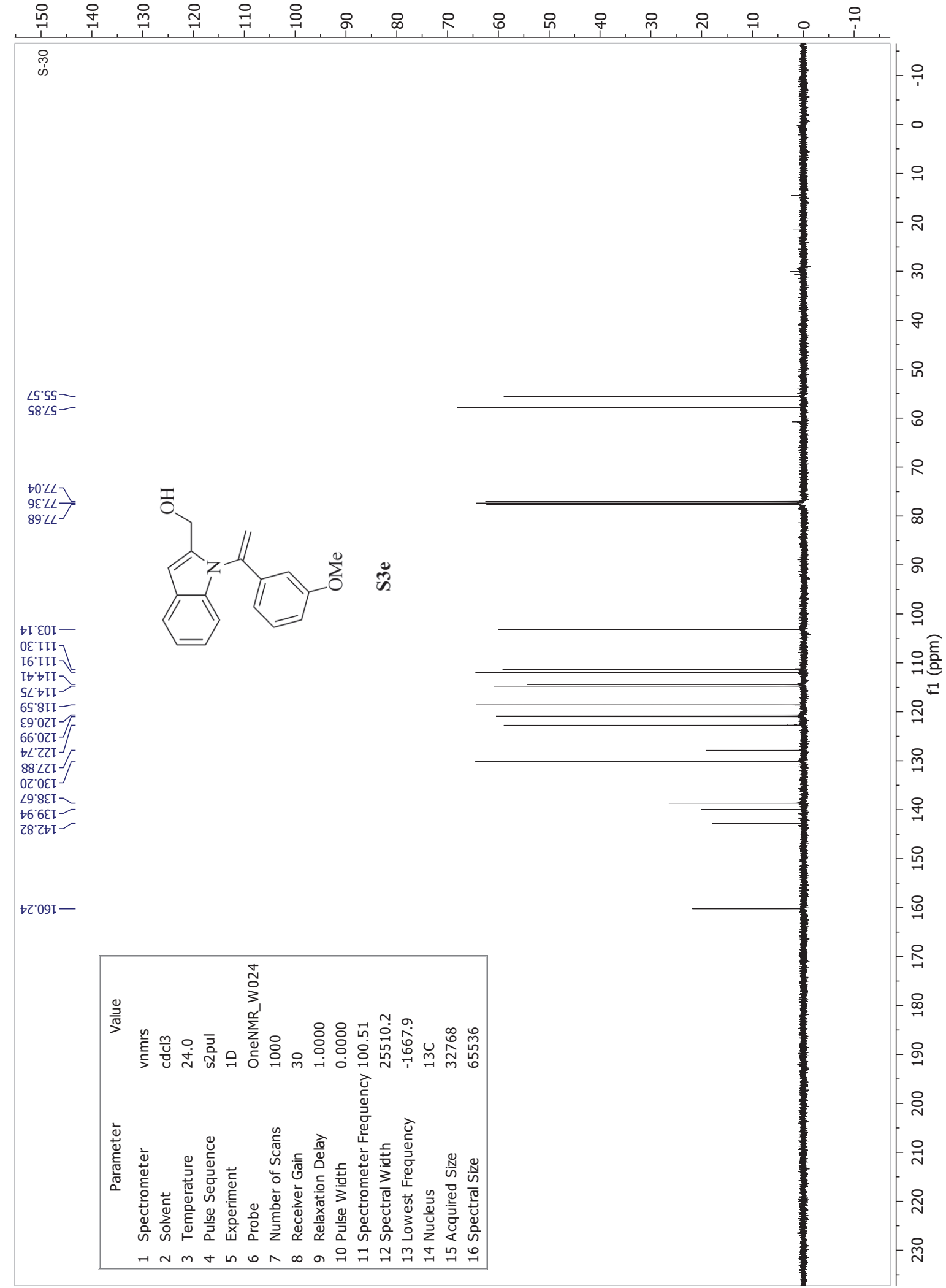


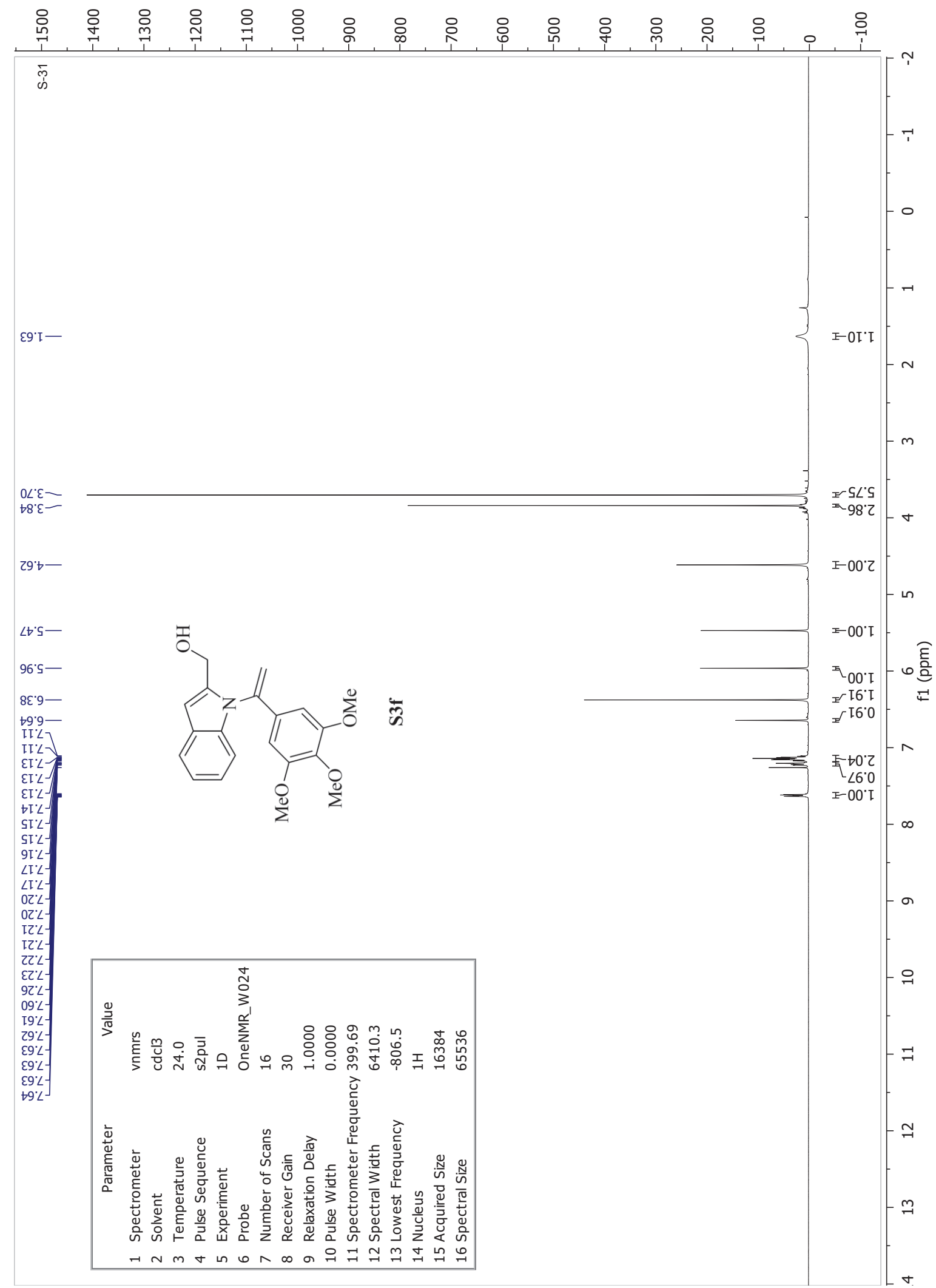




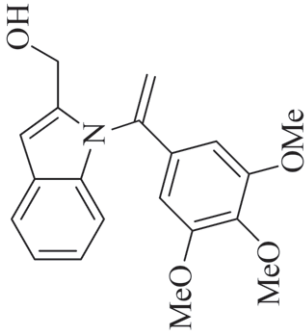




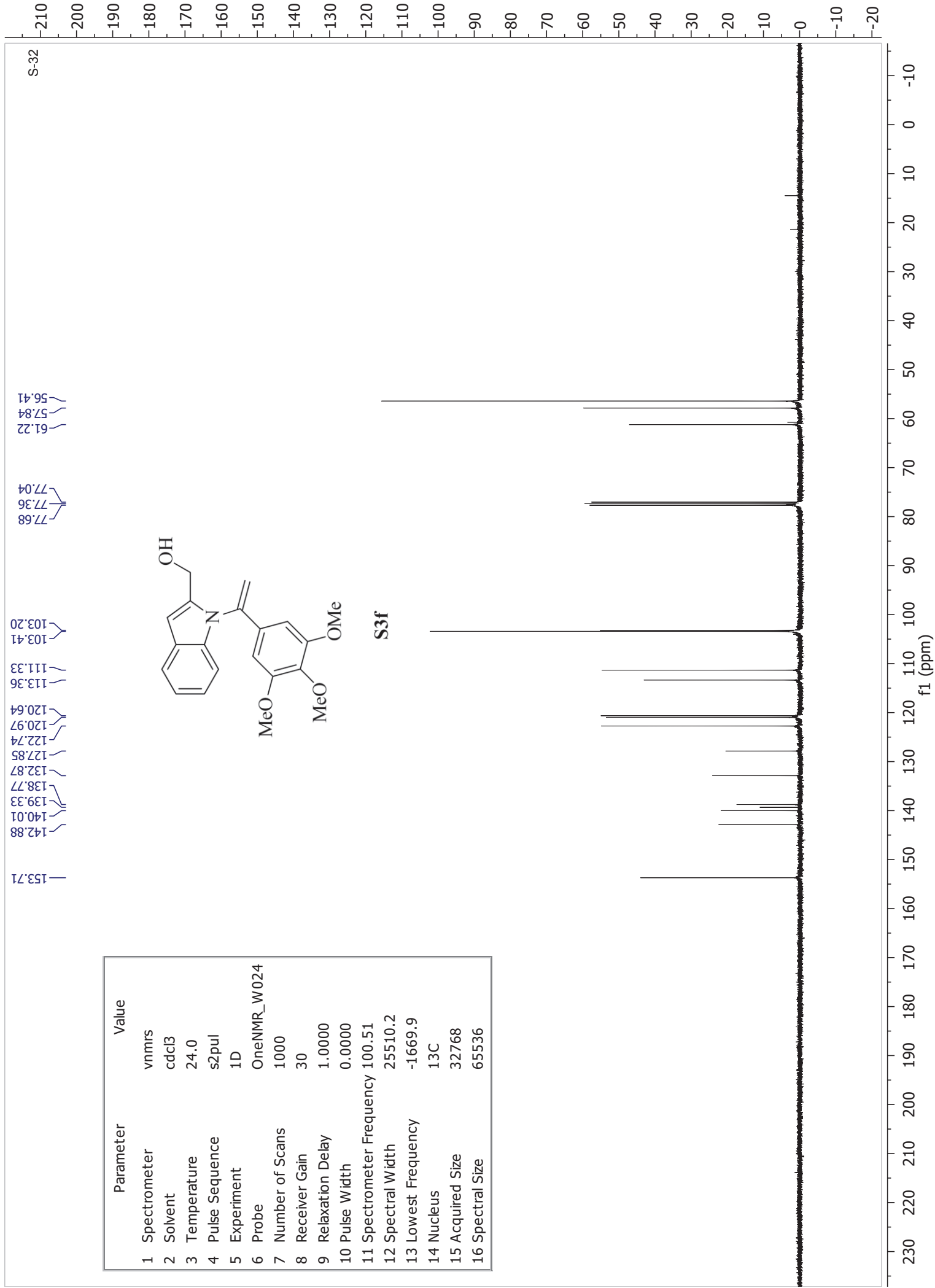




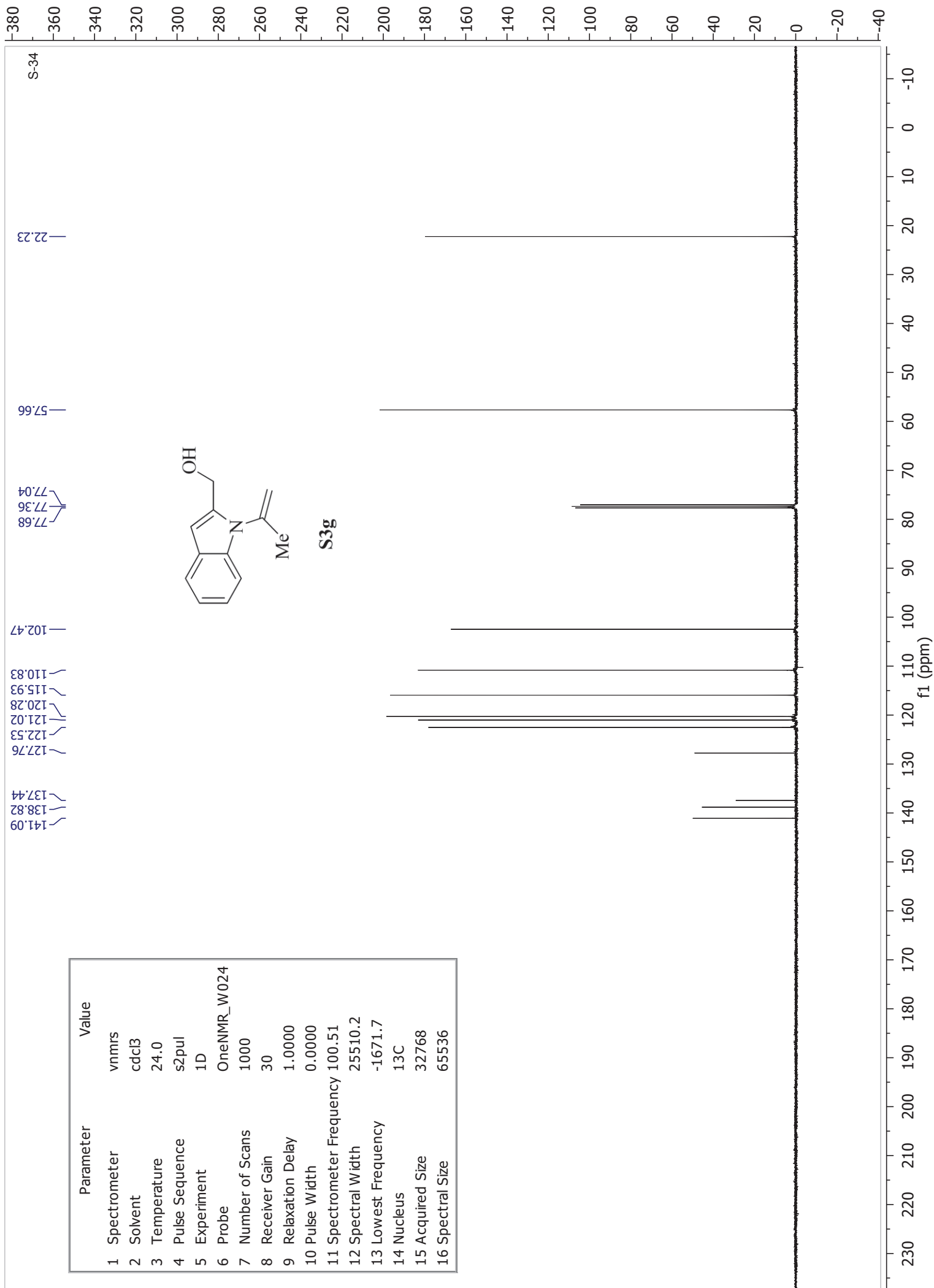
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9 Relaxation Delay	1.0000
10 Pulse Width	0.0000
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12 Spectral Width	25510.2
13 Lowest Frequency	-1669.9
14 Nucleus	¹³ C
15 Acquired Size	32768
16 Spectral Size	65536

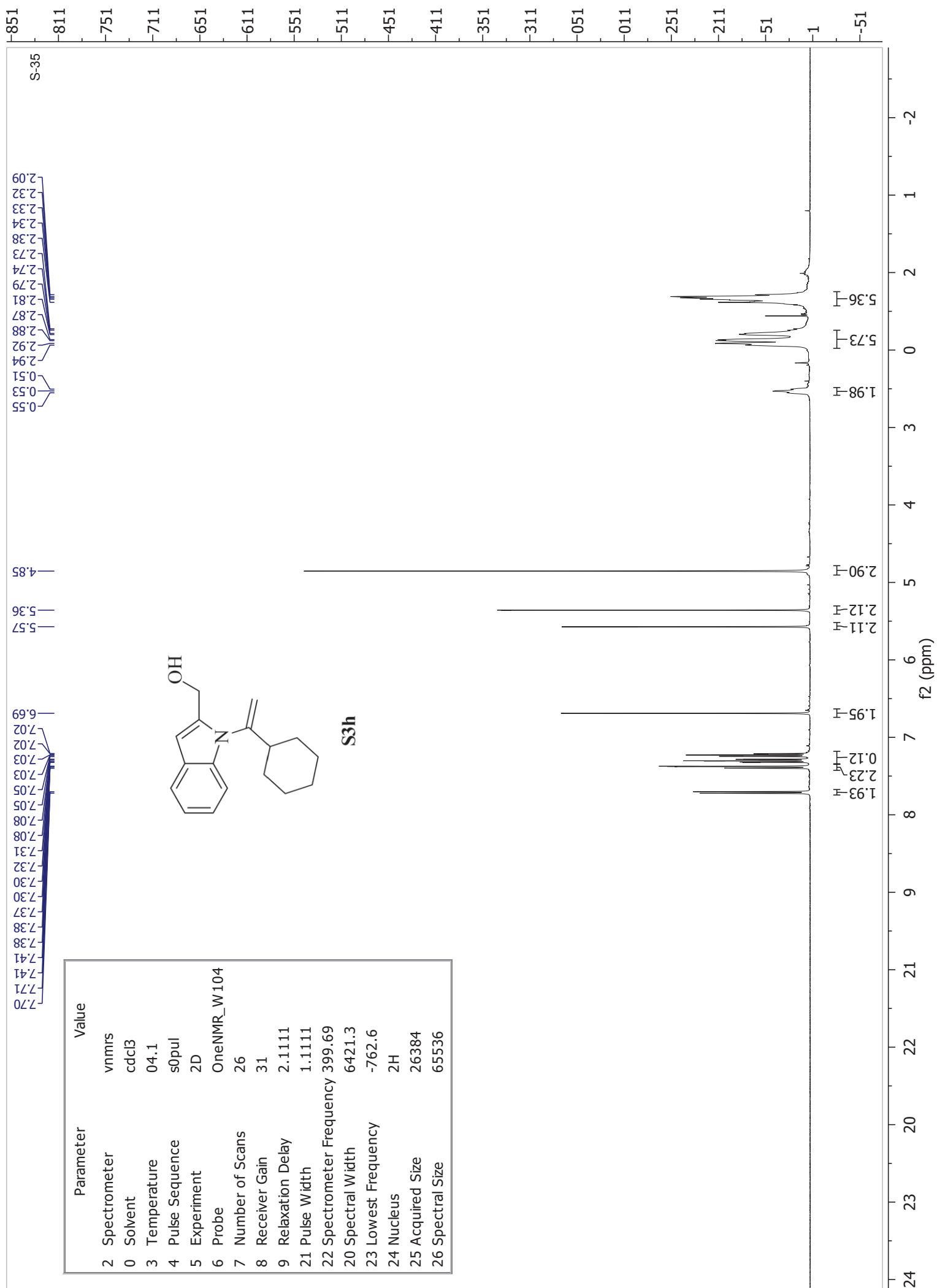


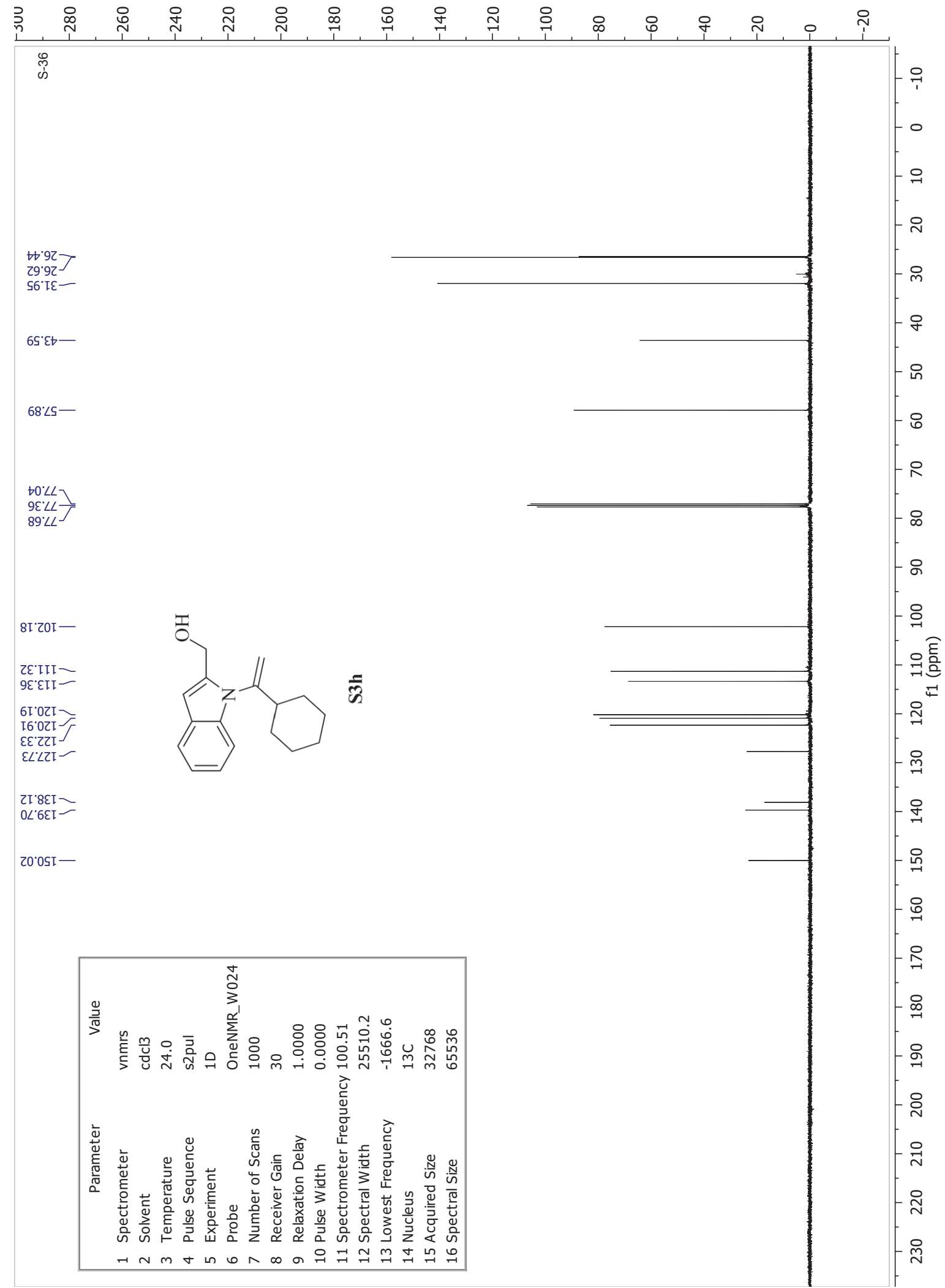
S3f

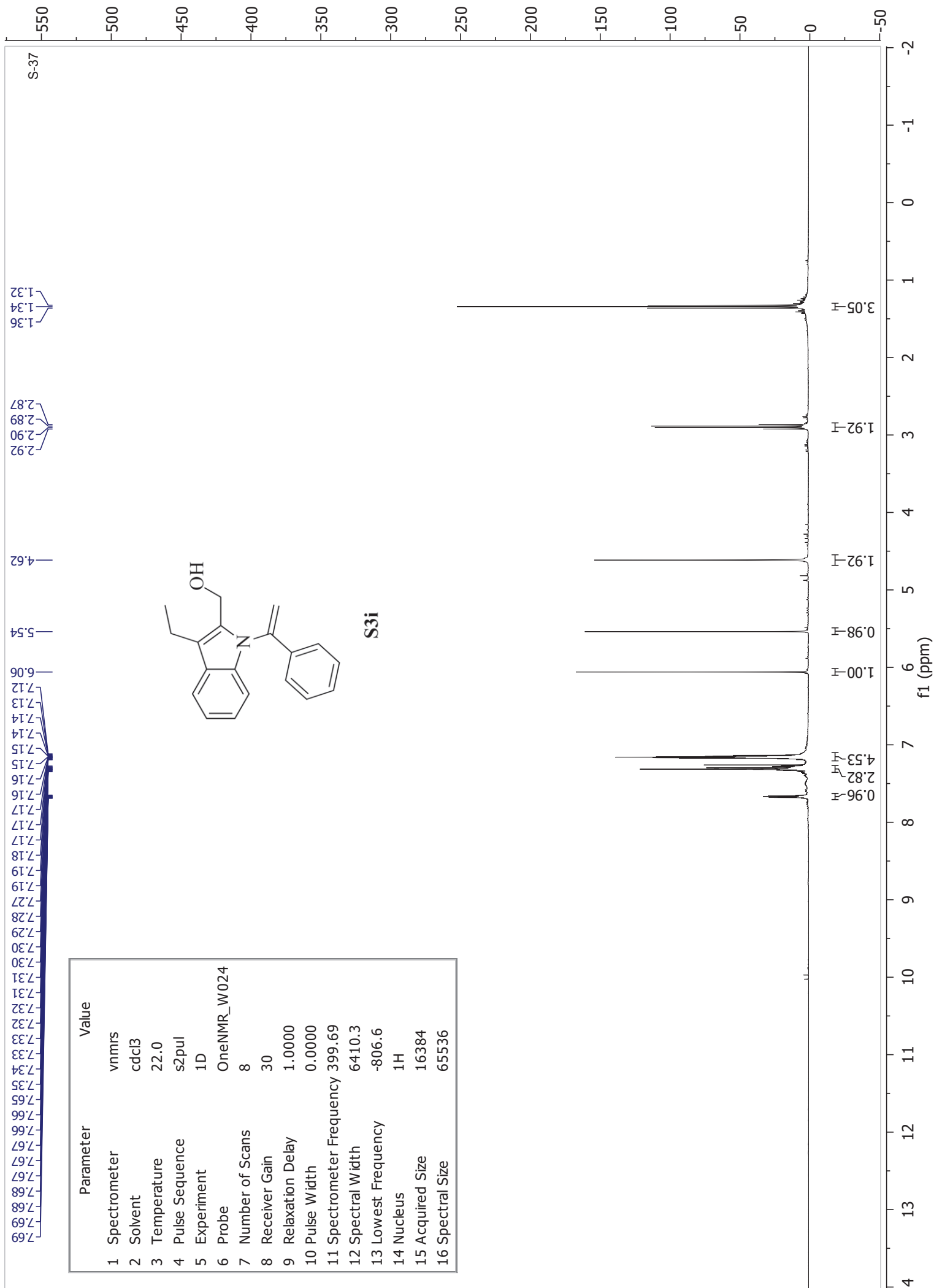


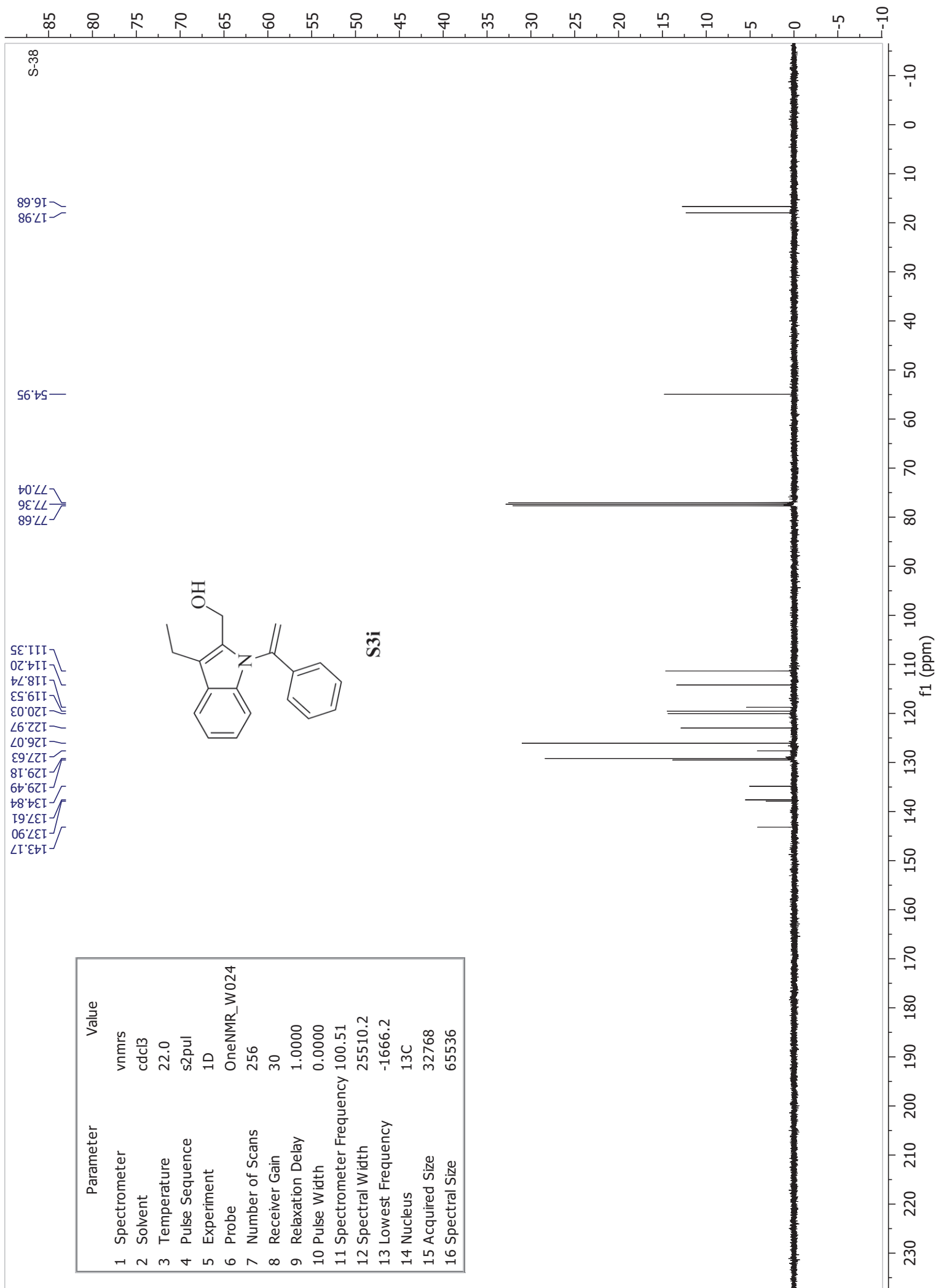


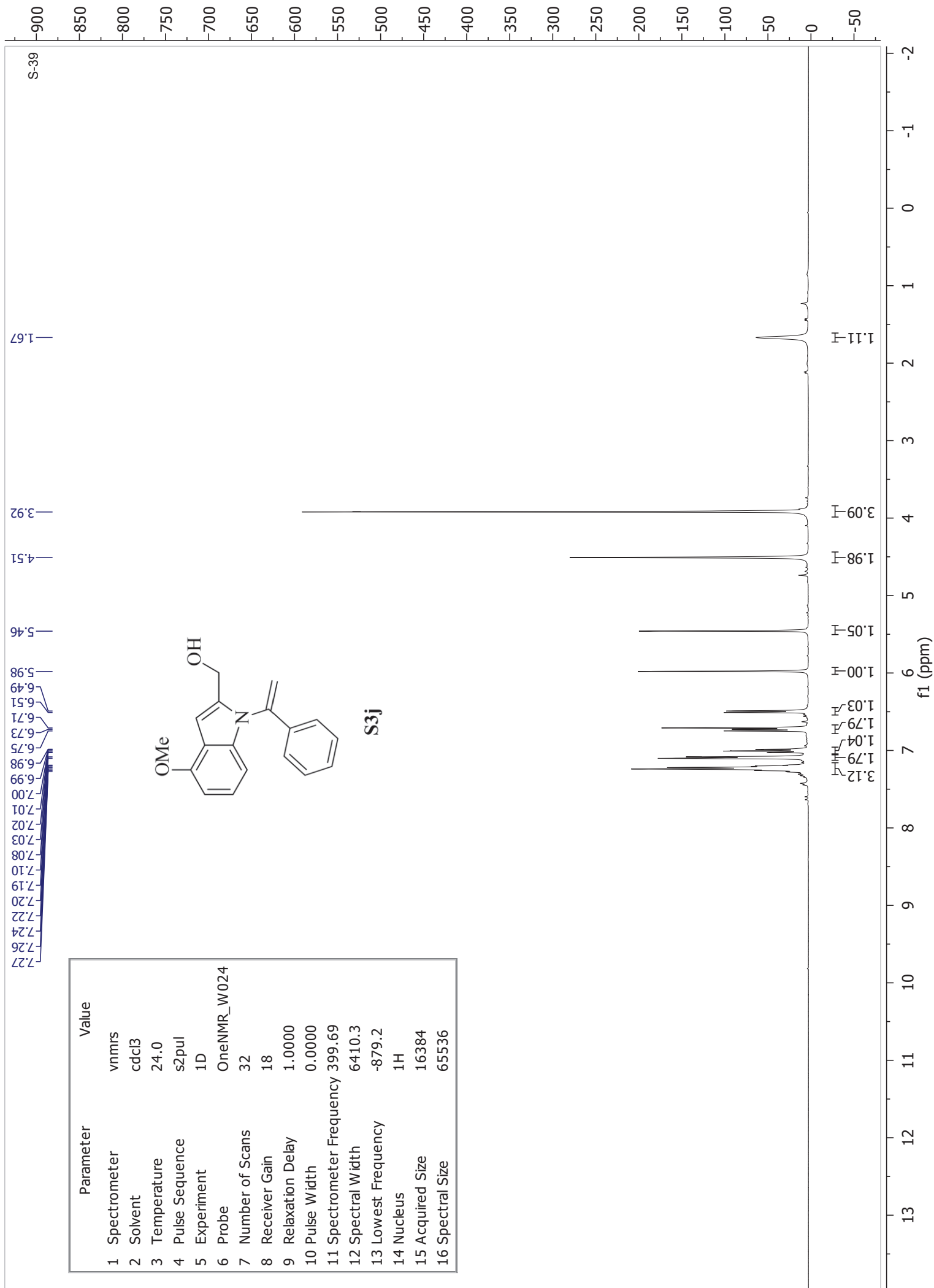




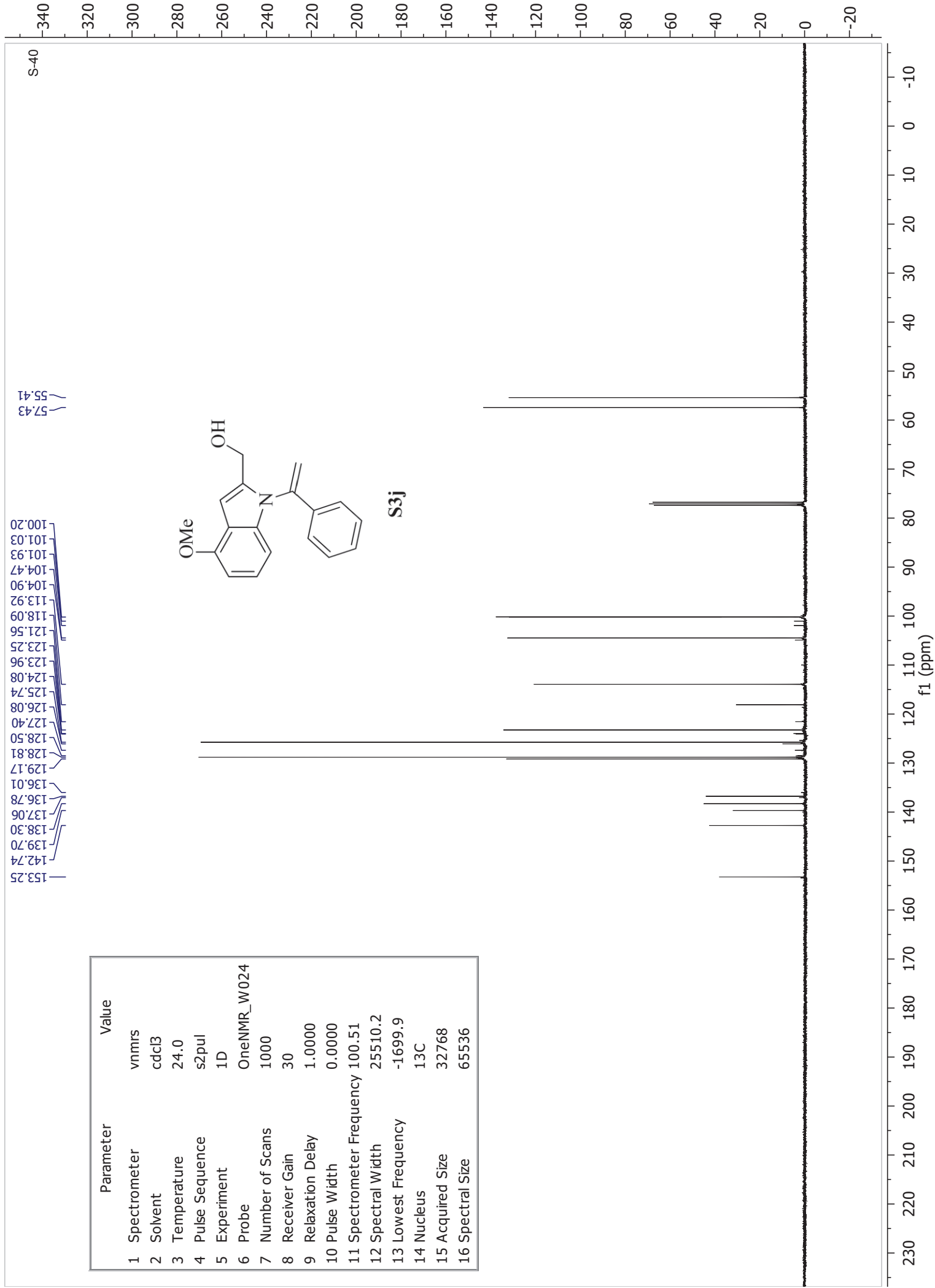


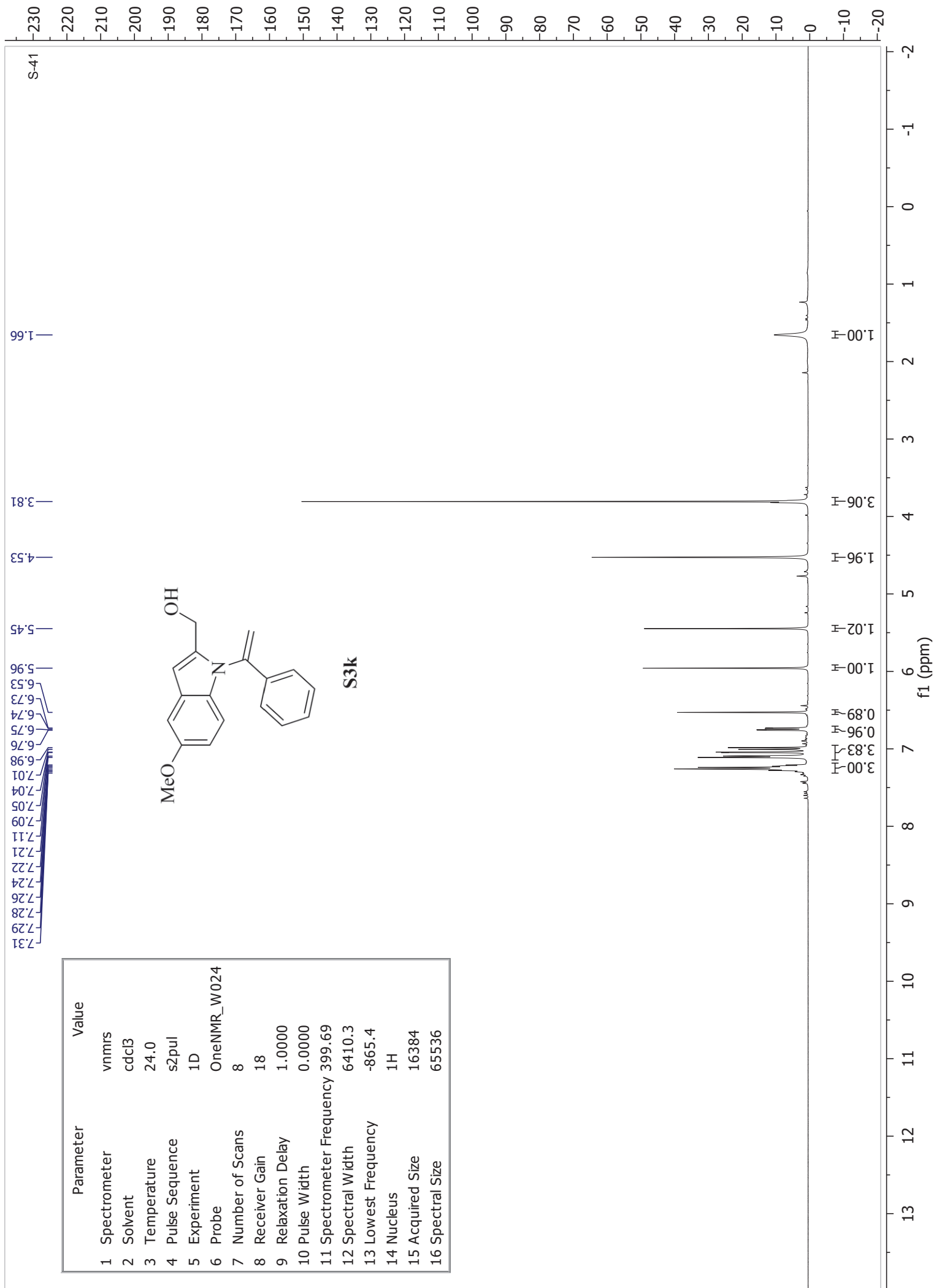




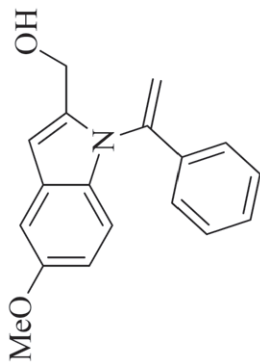


Parameter	Value
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2 Solvent	cdcl3
3 Temperature	24.0
4 Pulse Sequence	s2pul
5 Experiment	1D
6 Probe	OneNMR_W024
7 Number of Scans	1000
8 Receiver Gain	30
9 Relaxation Delay	1.0000
10 Pulse Width	0.0000
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12 Spectral Width	25510.2
13 Lowest Frequency	-1699.9
14 Nucleus	¹³ C
15 Acquired Size	32768
16 Spectral Size	65536

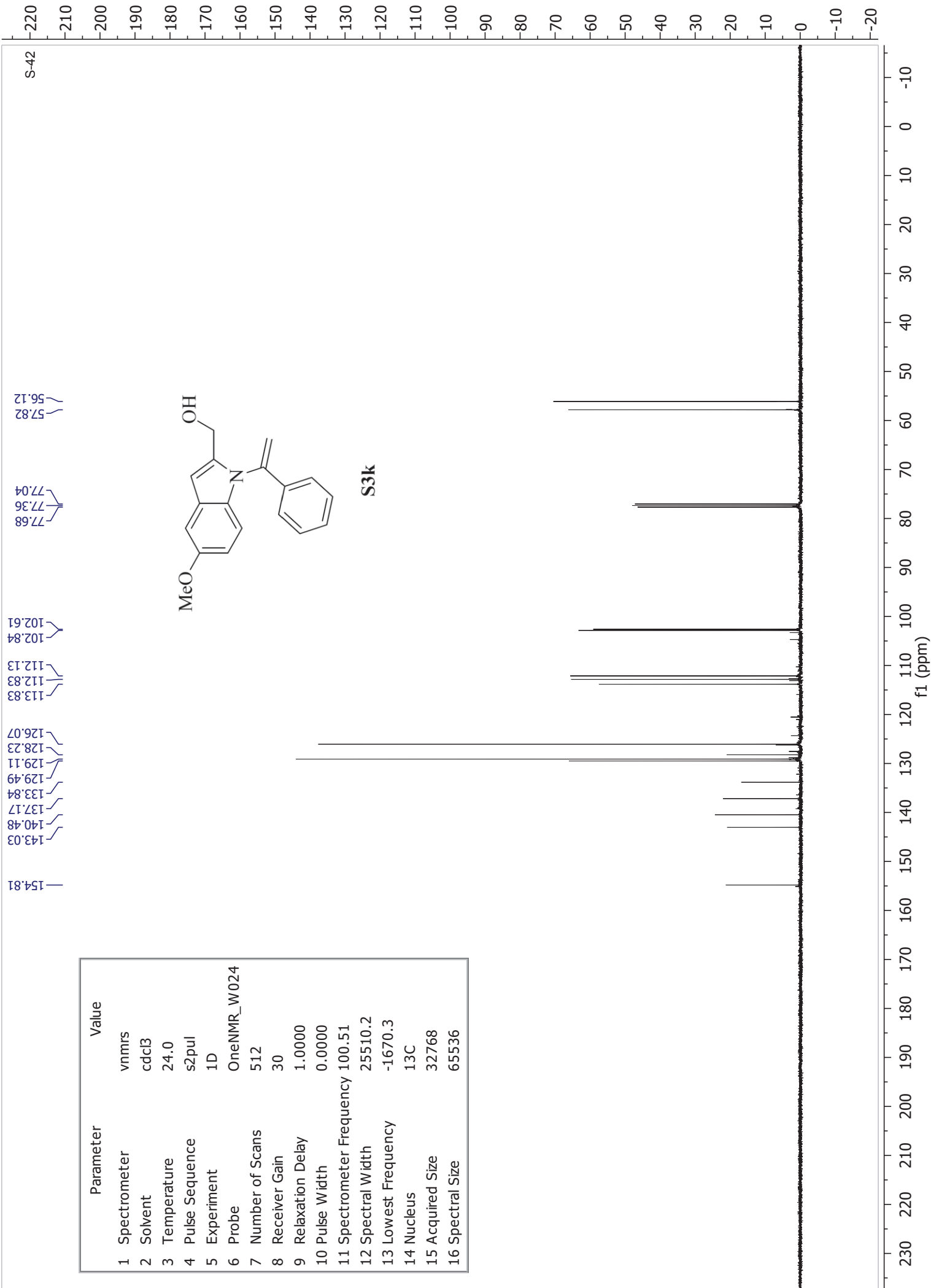


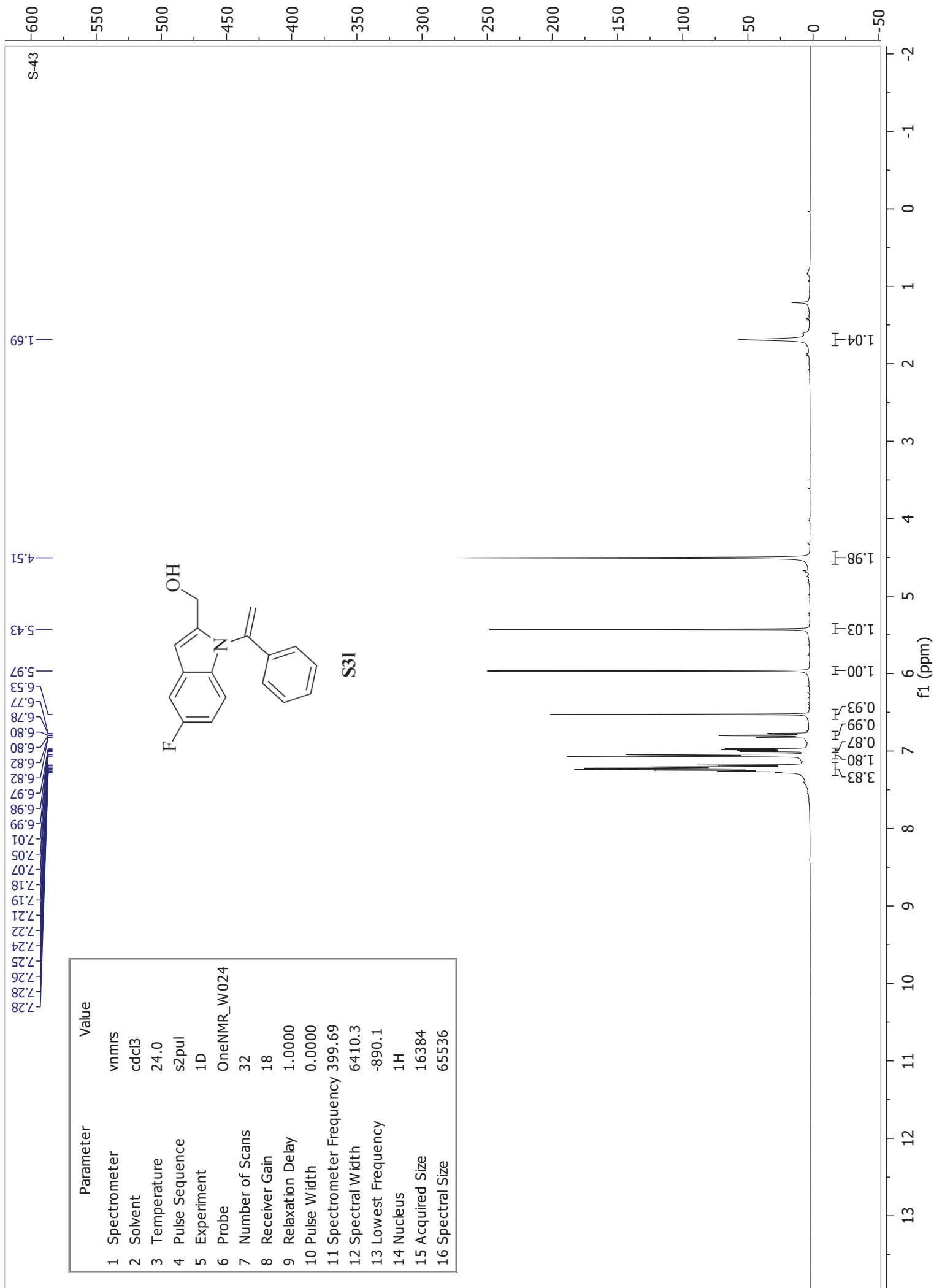


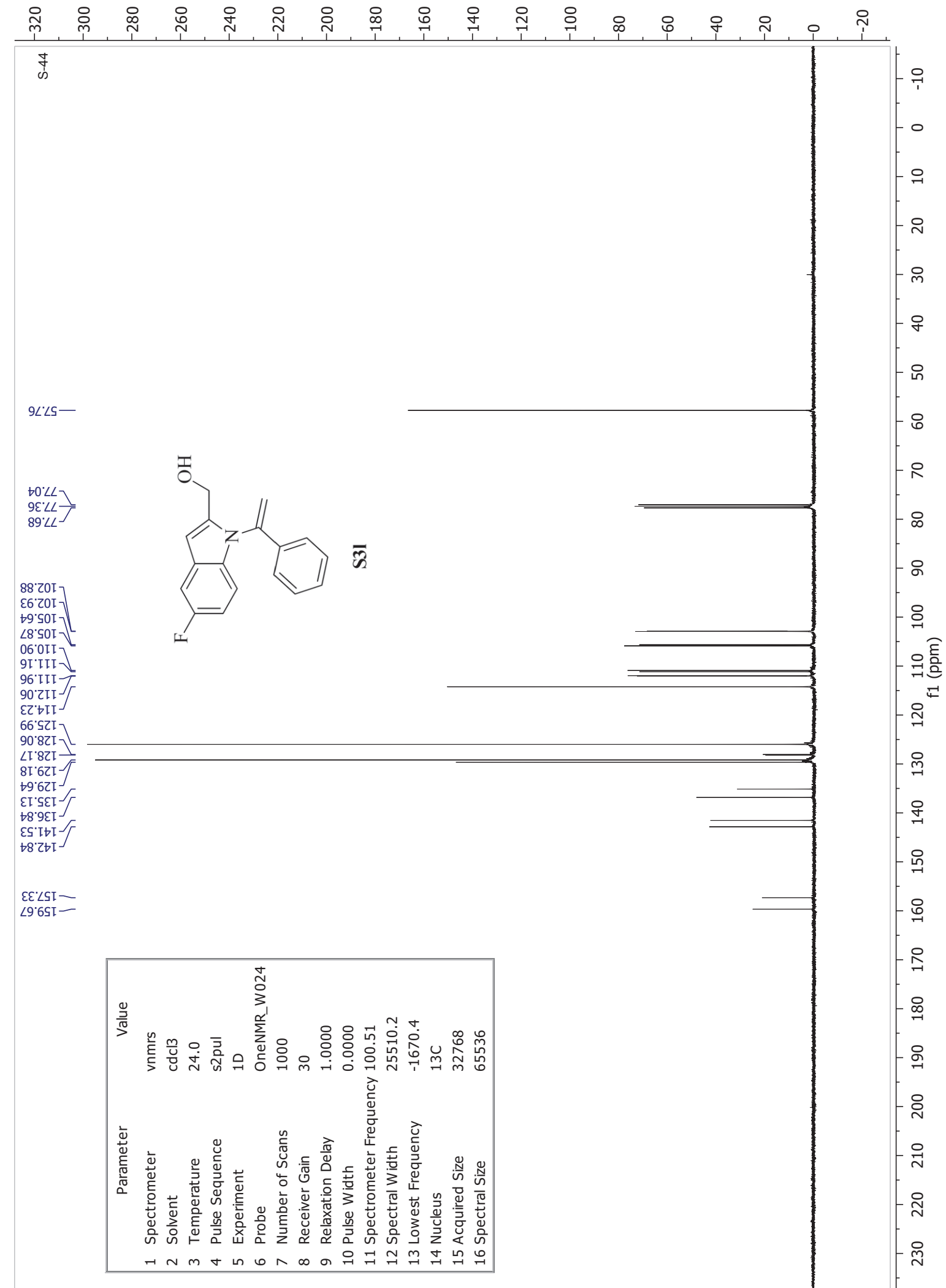
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16 Spectral Size	65536

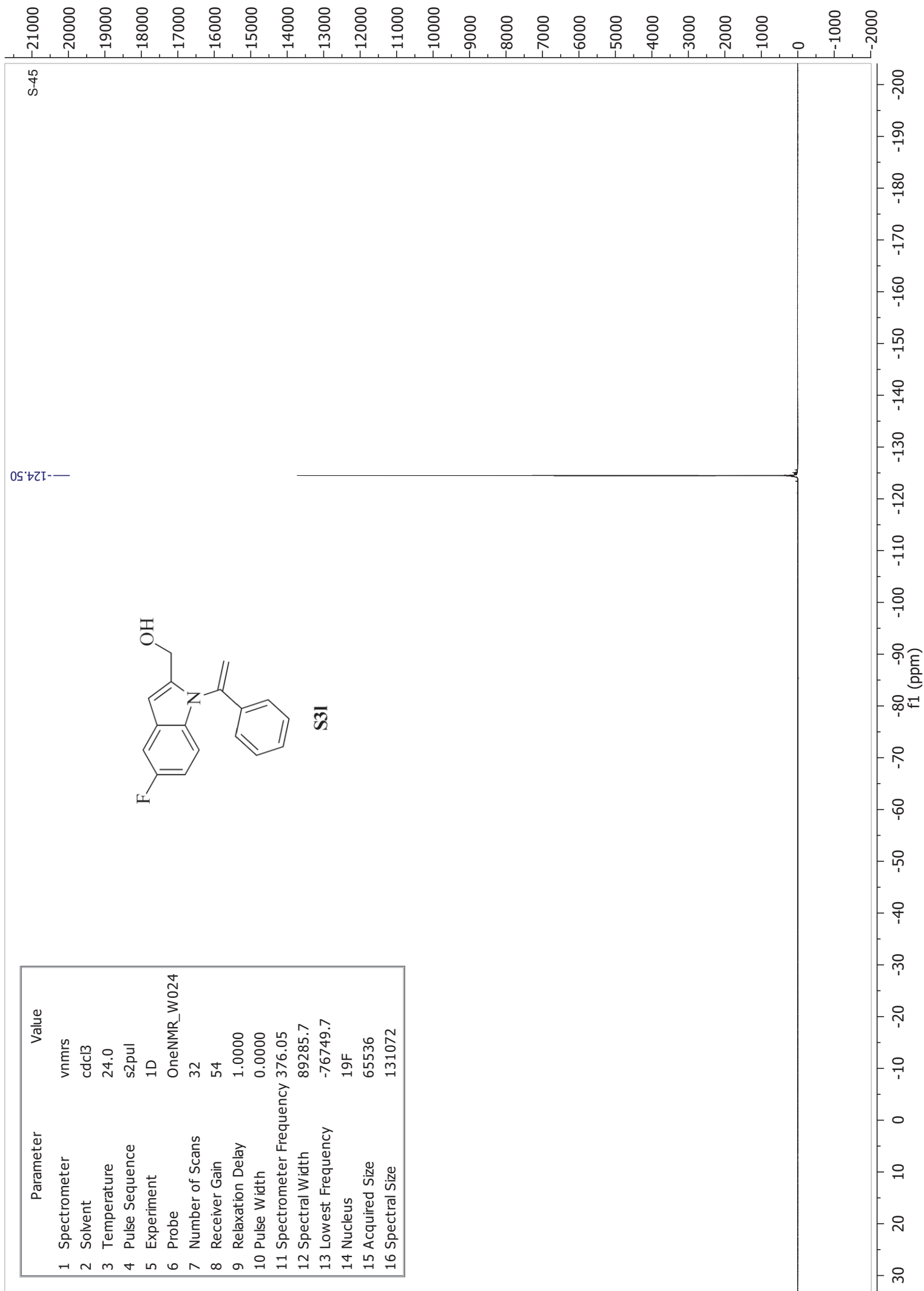


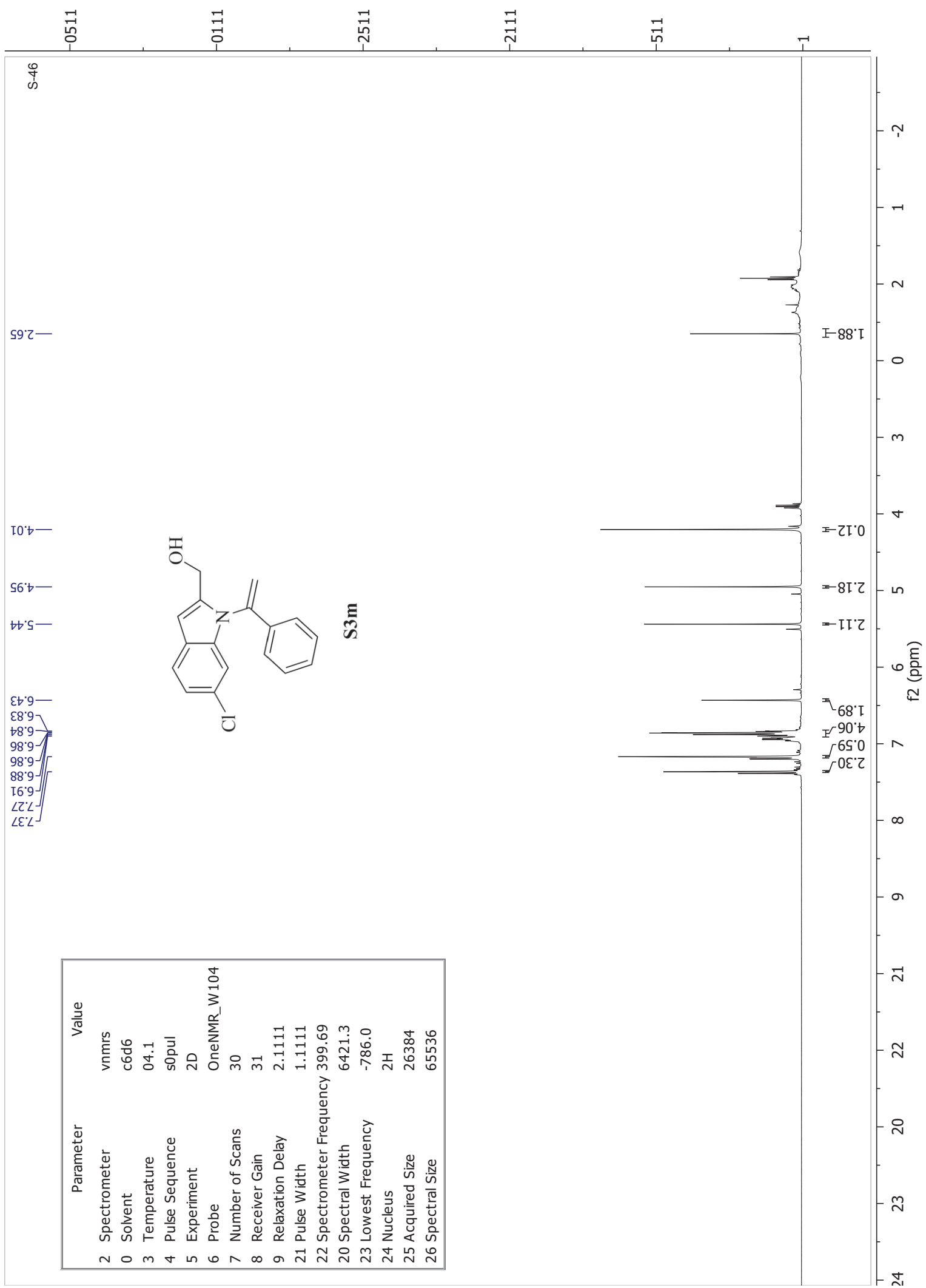
S3k

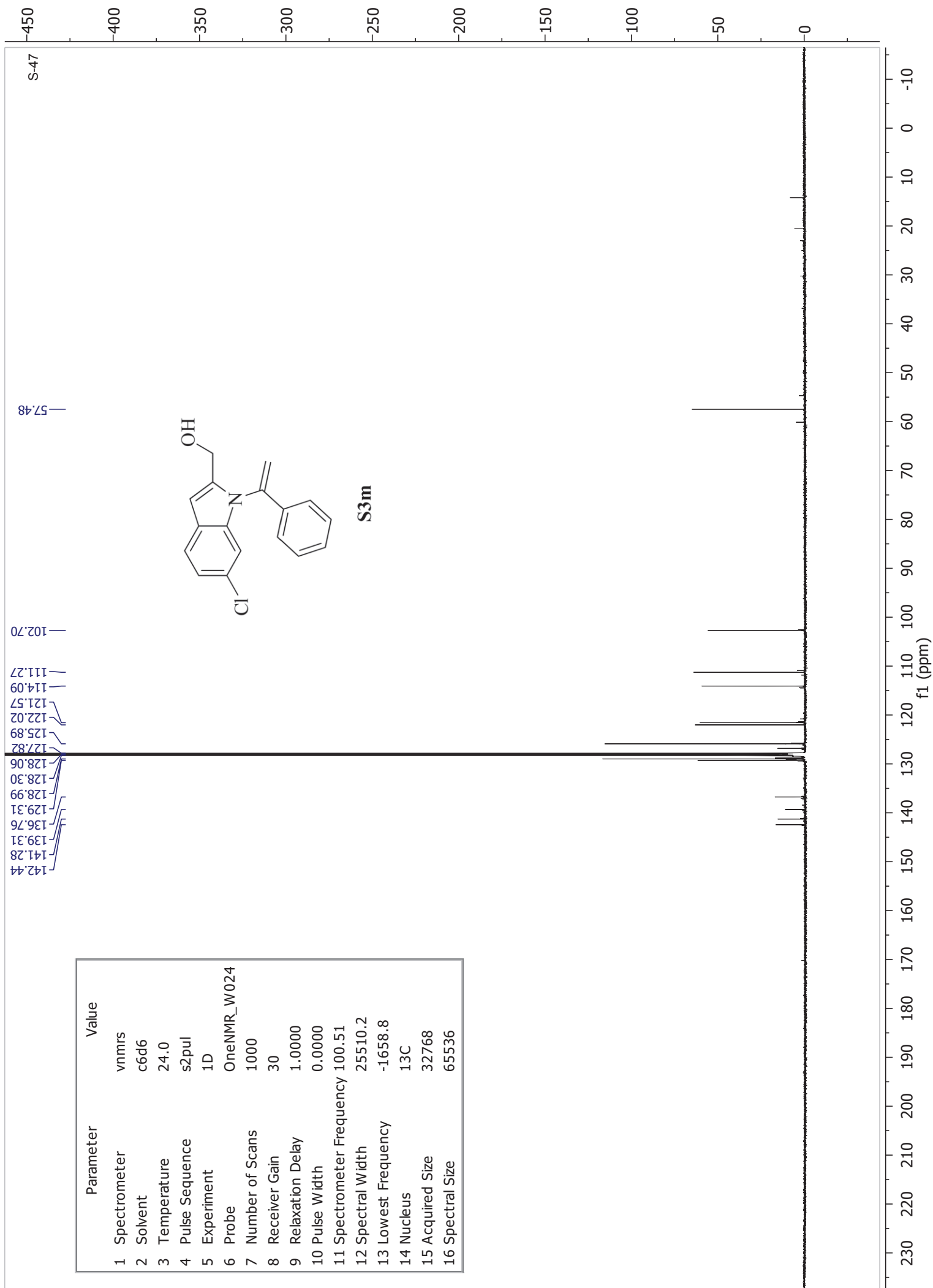




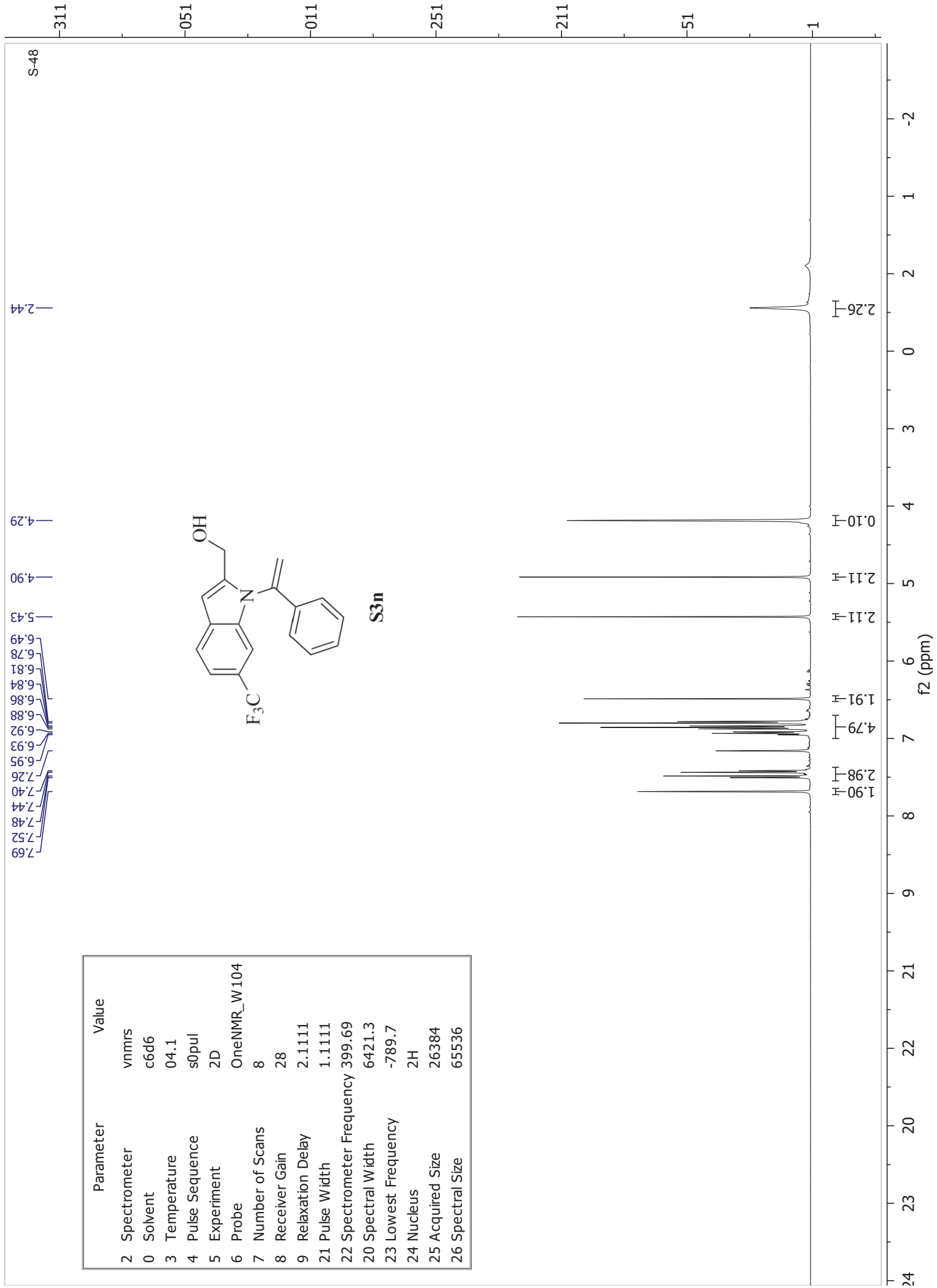


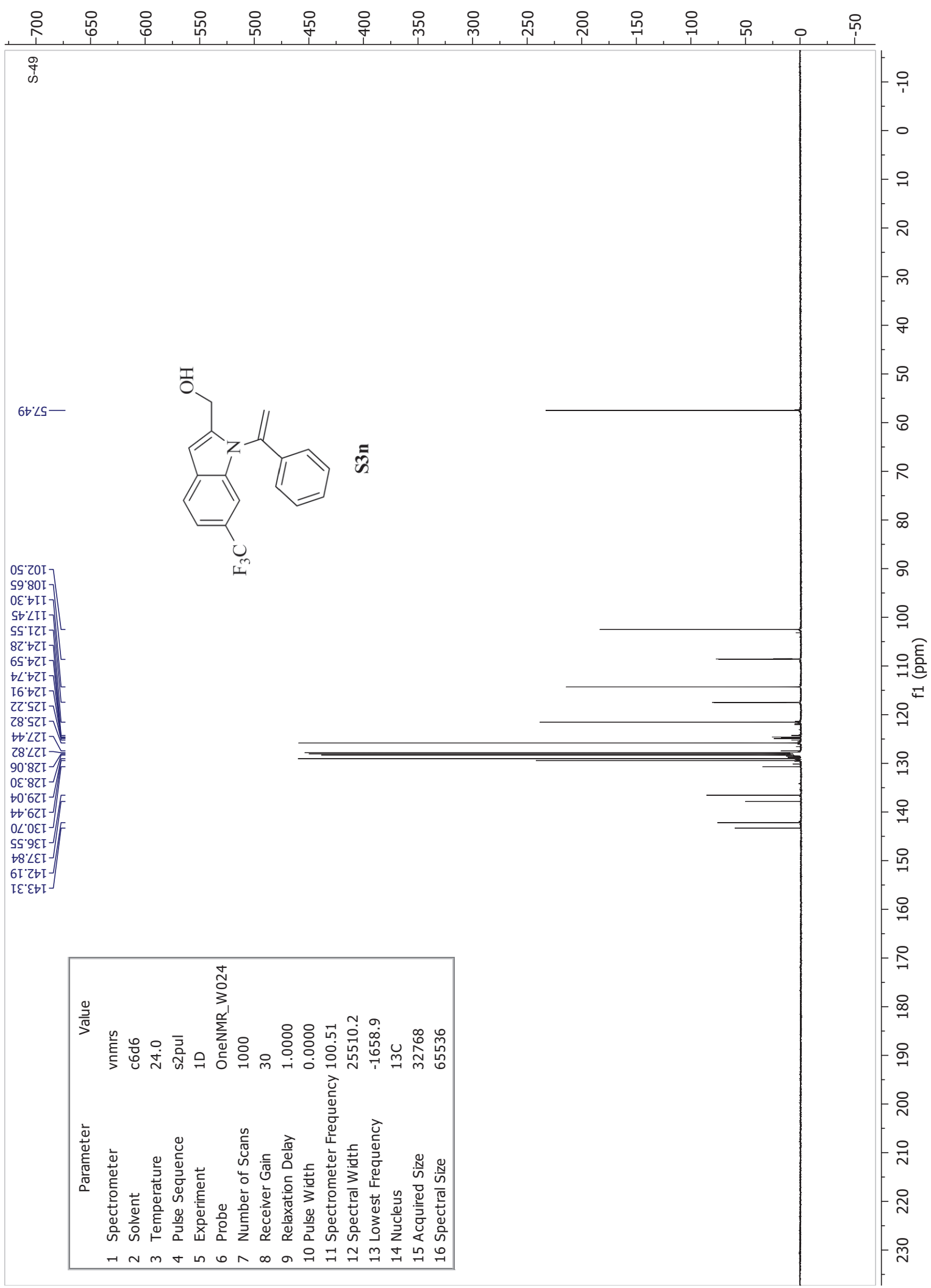


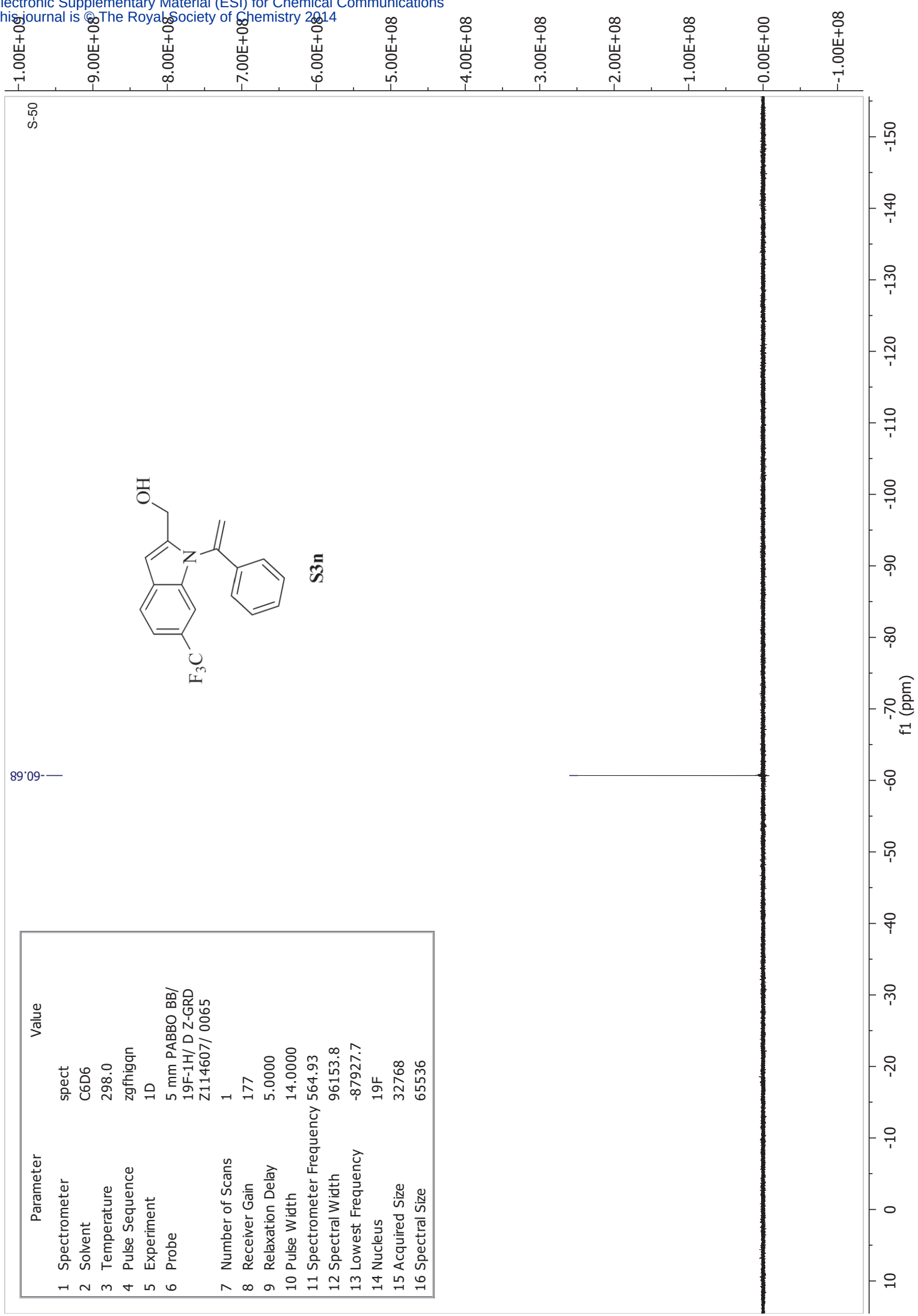


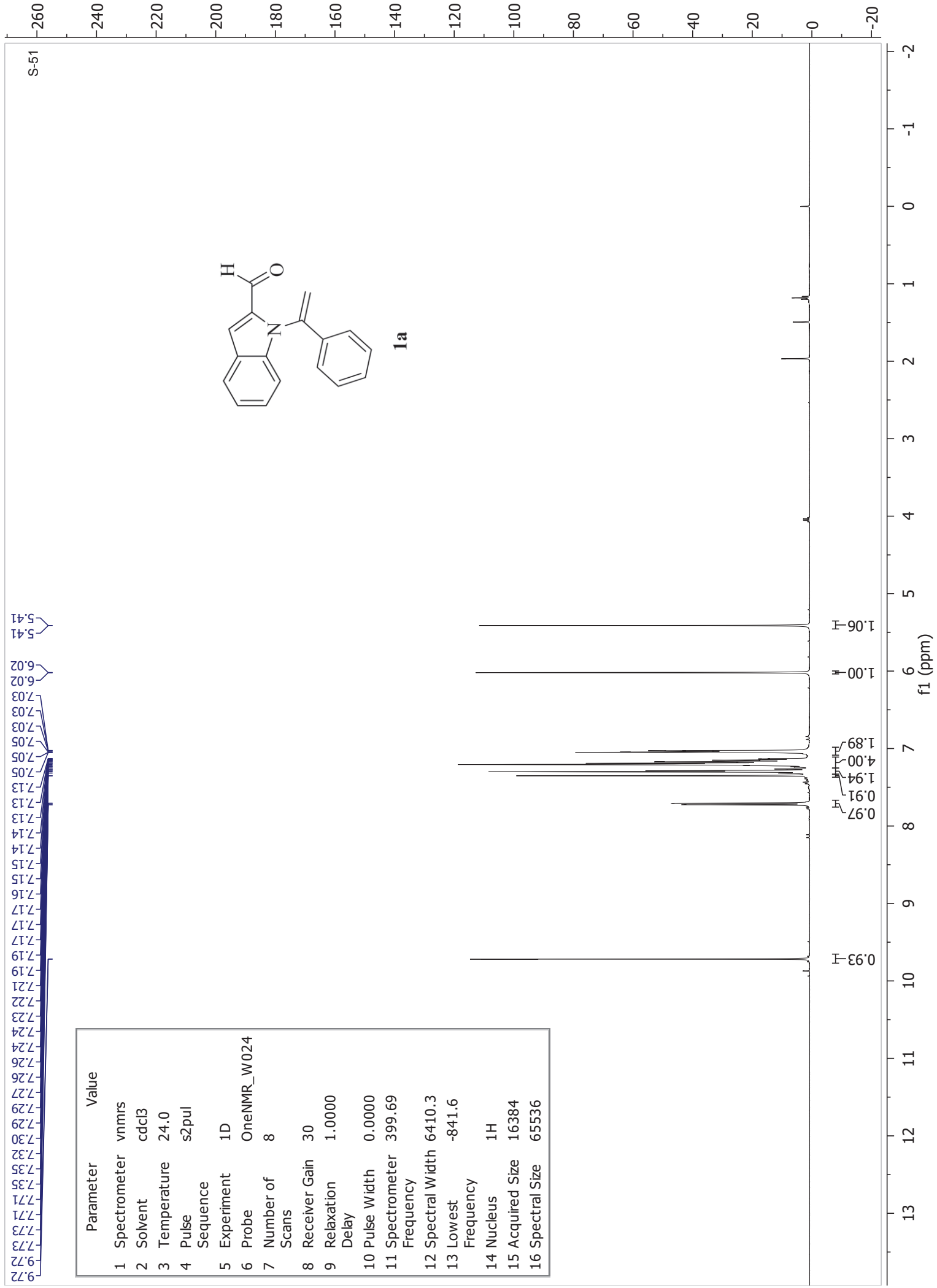


Parameter	Value
2 Spectrometer	nmrs
0 Solvent	c6d6
3 Temperature	04.1
4 Pulse Sequence	s0pul
5 Experiment	2D
6 Probe	OneNMR_W104
7 Number of Scans	8
8 Receiver Gain	28
9 Relaxation Delay	2.111
21 Pulse Width	1.111
22 Spectrometer Frequency	399.69
20 Spectral Width	6421.3
23 Lowest Frequency	-789.7
24 Nucleus	² H
25 Acquired Size	26384
26 Spectral Size	65536

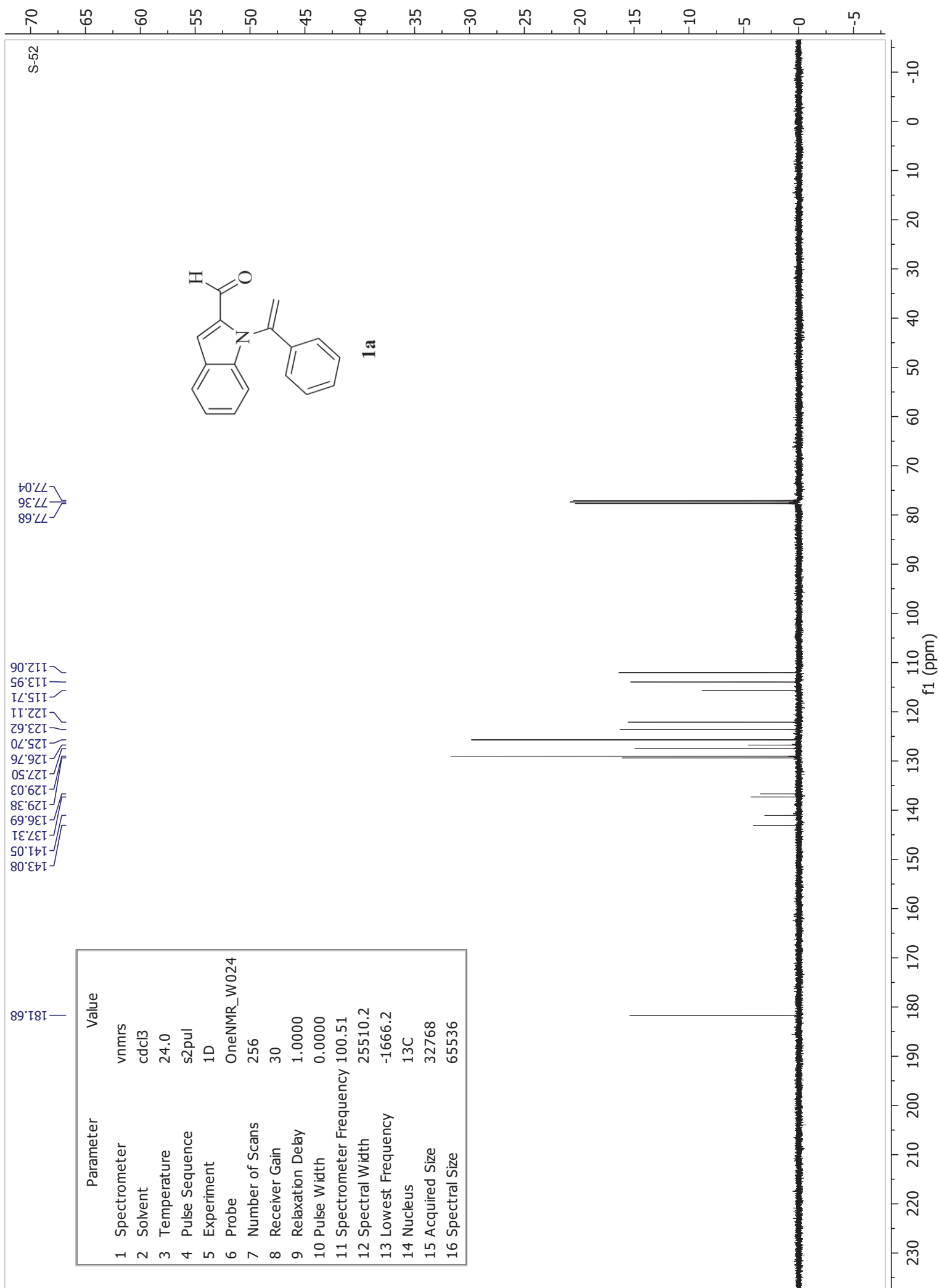


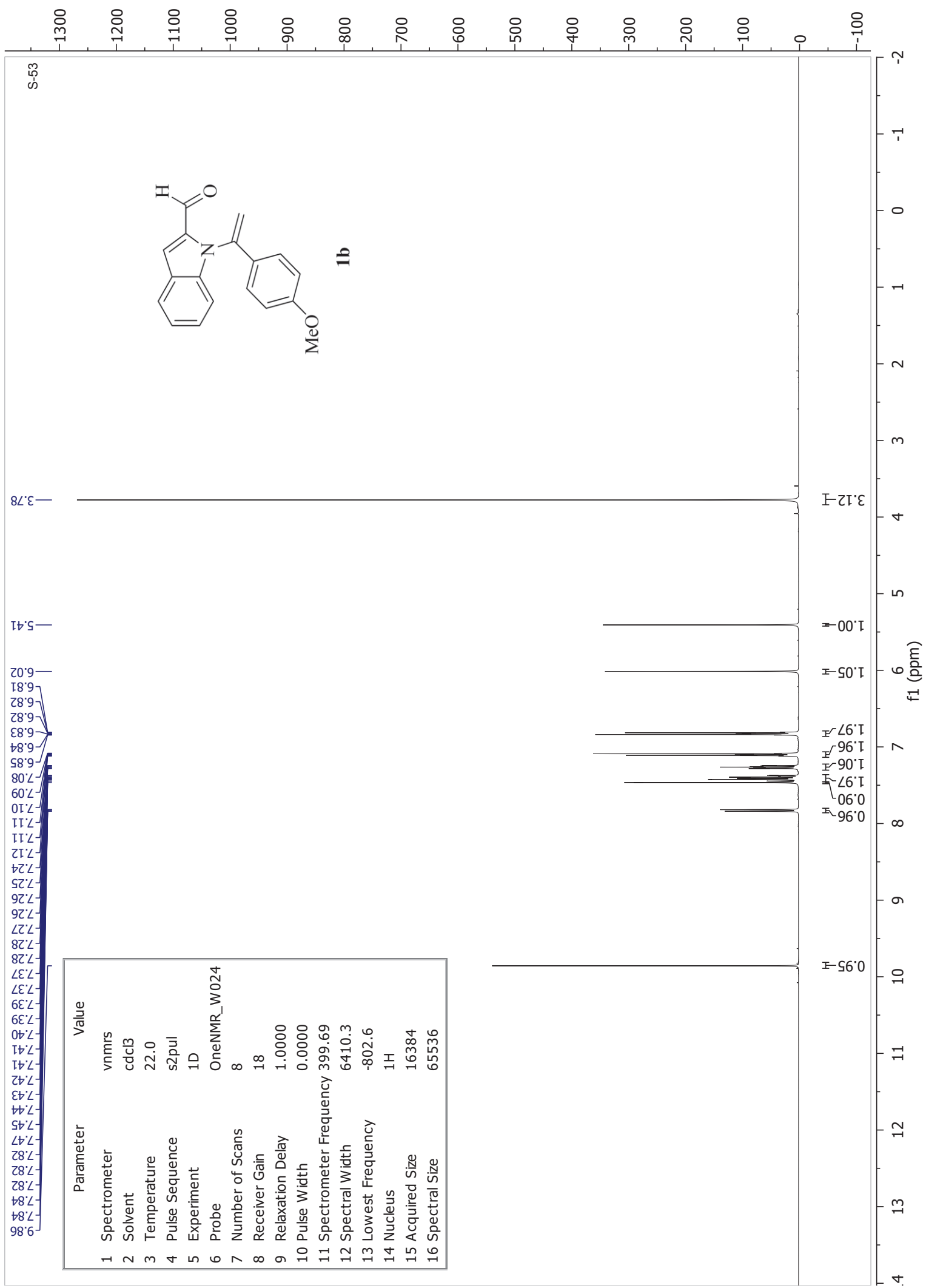


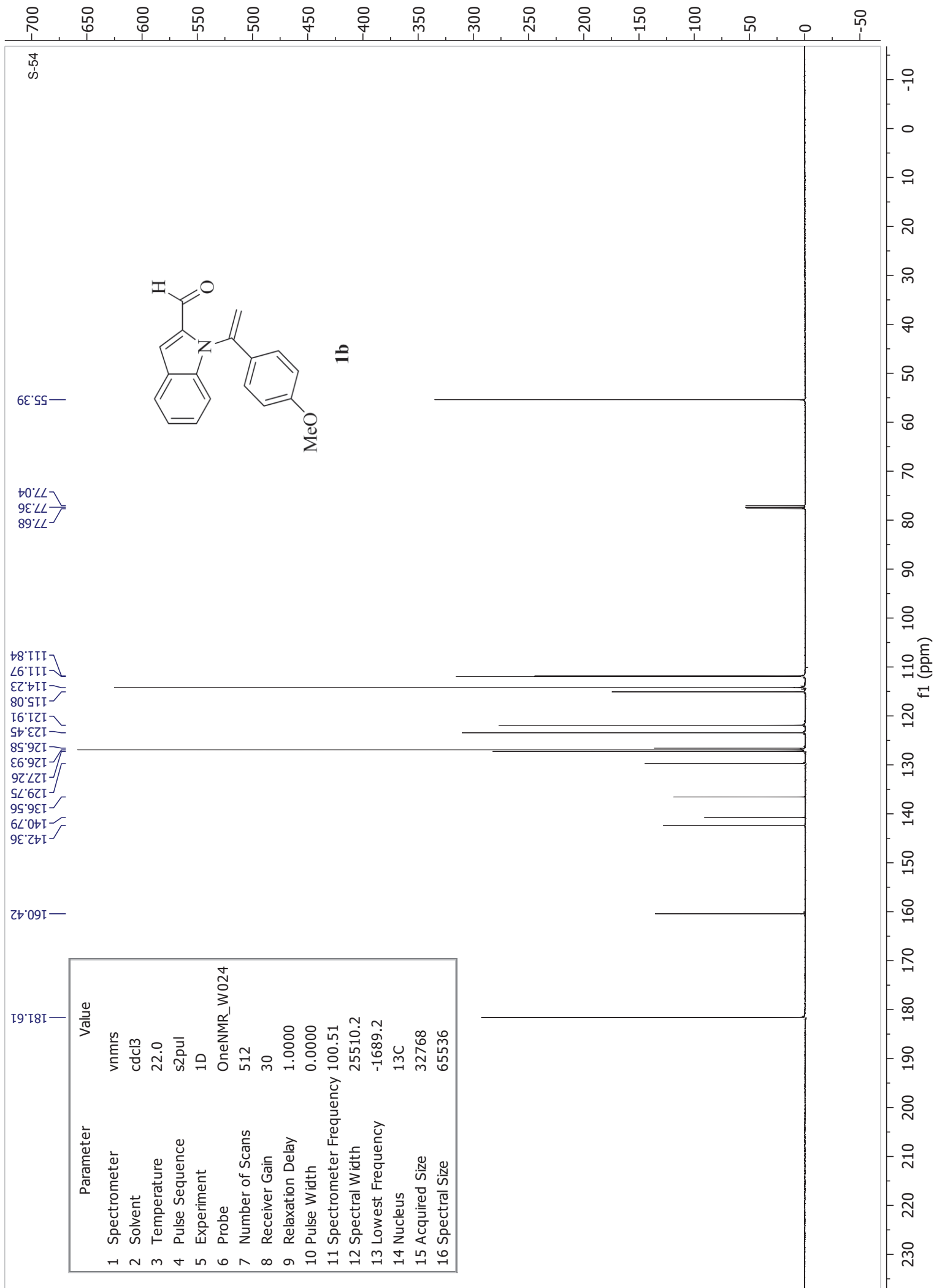


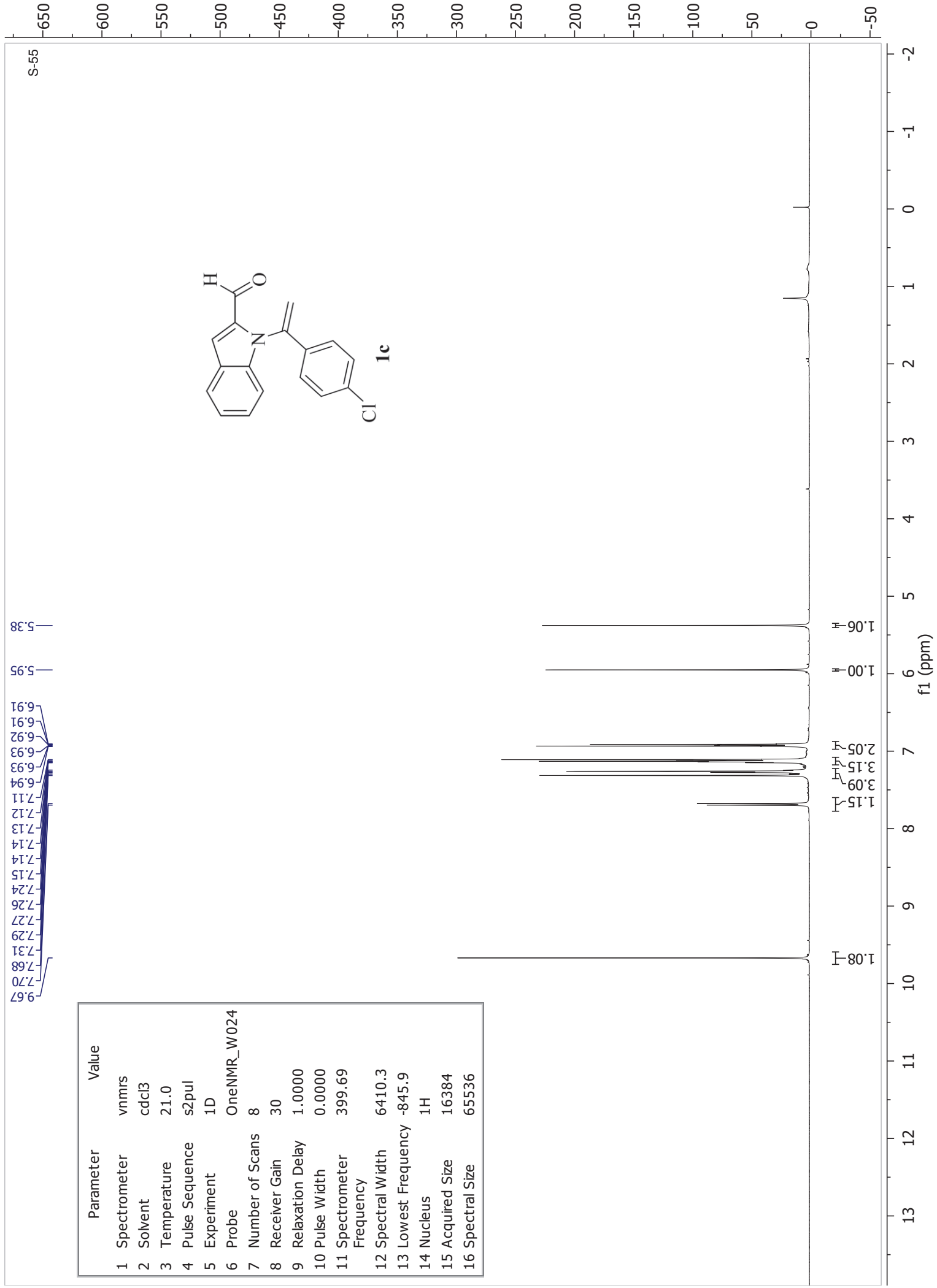


Parameter	Value
1 Spectrometer	vmrns
2 Solvent	cdcl3
3 Temperature	24.0
4 Pulse Sequence	s2pul
5 Experiment	1D
6 Probe	OneNMR_W024
7 Number of Scans	8
8 Receiver Gain	30
9 Relaxation Delay	1.0000
10 Pulse Width	0.0000
11 Spectrometer Frequency	399.69
12 Spectral Width	6410.3
13 Lowest Frequency	-841.6
14 Nucleus	1H
15 Acquired Size	16384
16 Spectral Size	65536

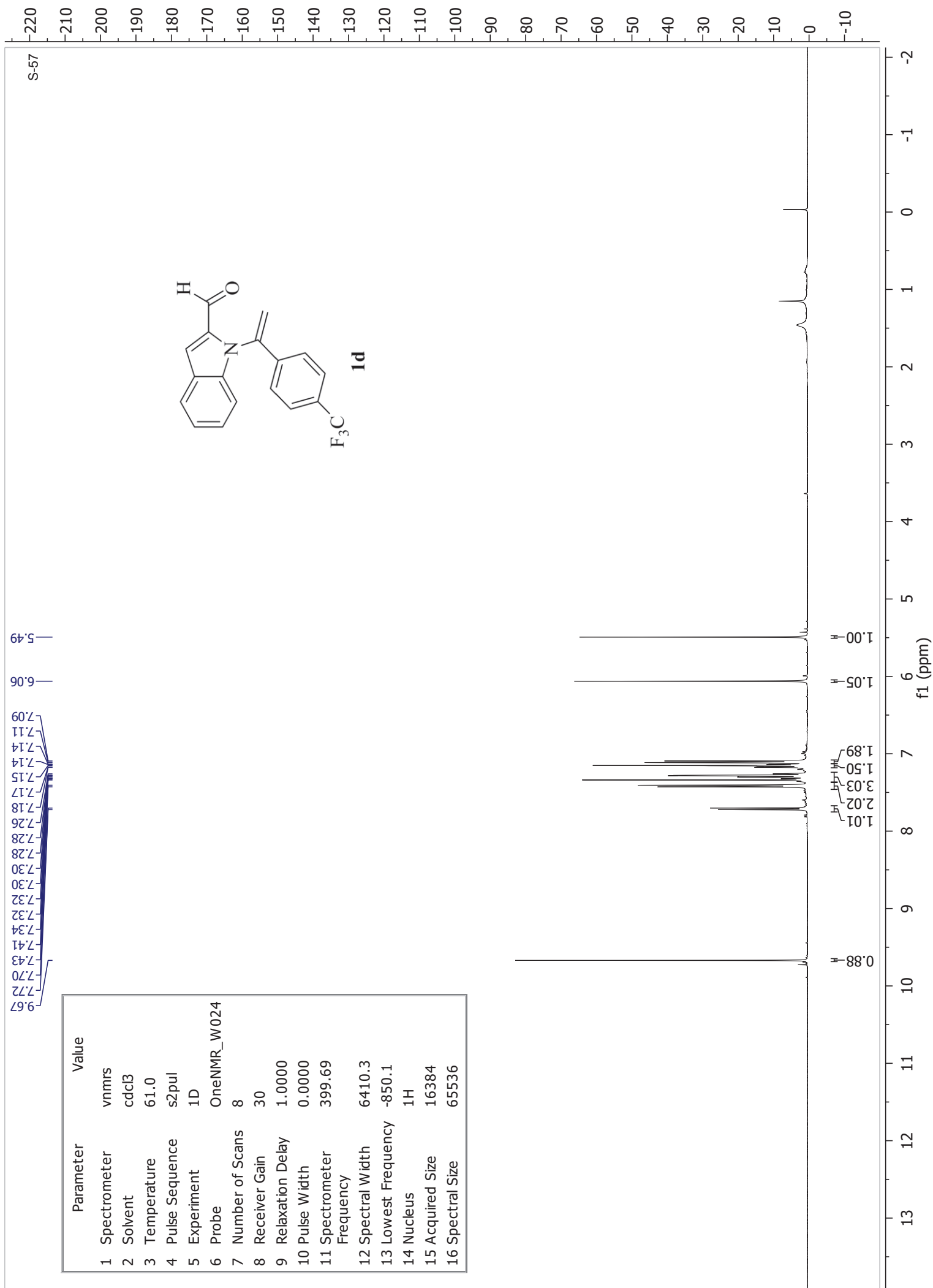


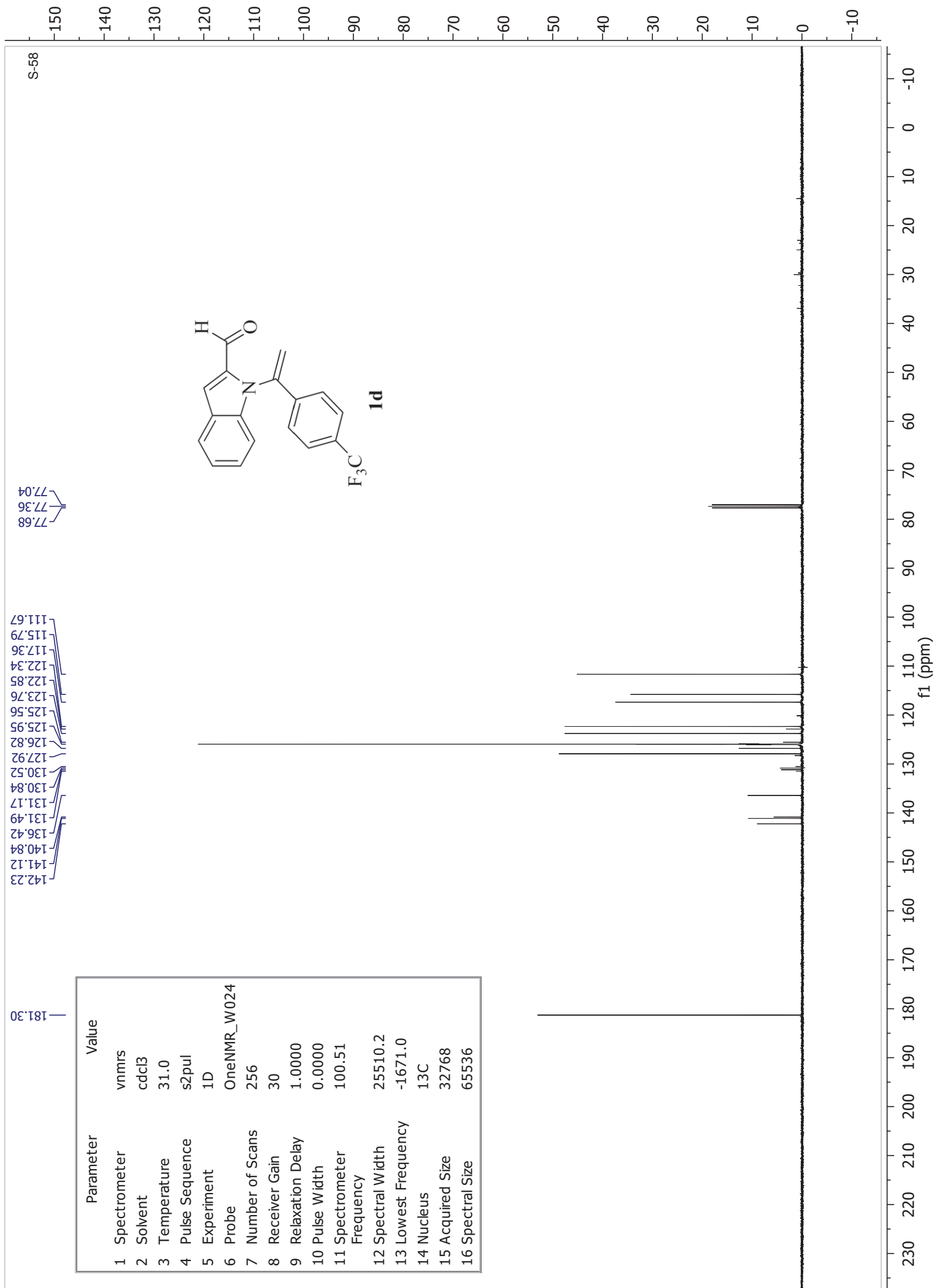






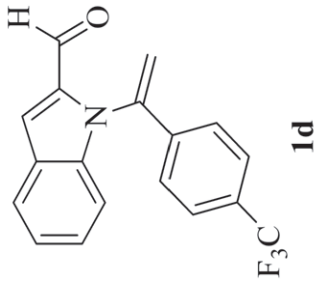






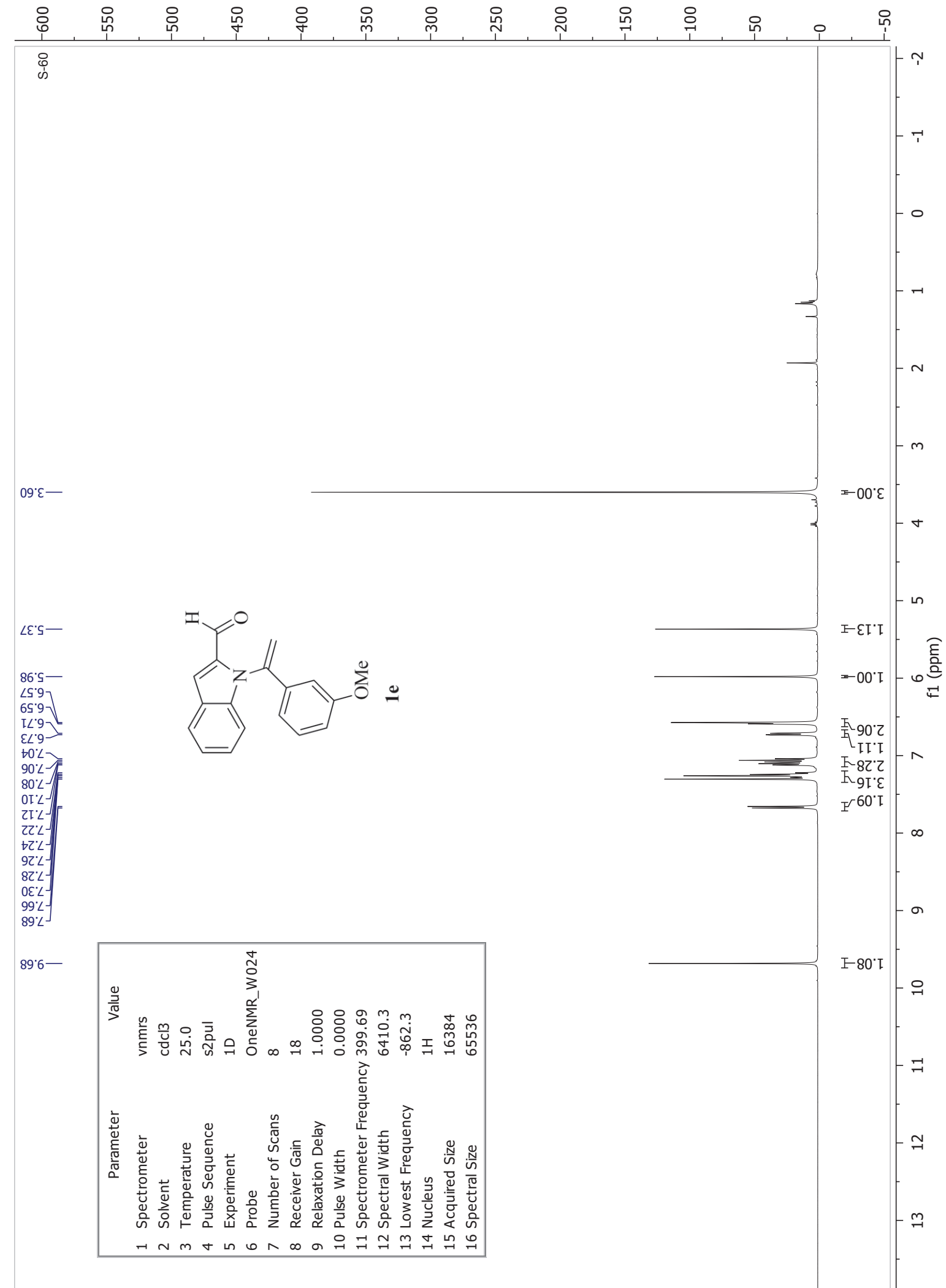
— 63.10

Parameter	Value
1 Spectrometer	vnmr5
2 Solvent	cdcl3
3 Temperature	61.0
4 Pulse Sequence	s2pul
5 Experiment	1D
6 Probe	OneNMR_W024
7 Number of Scans	16
8 Receiver Gain	56
9 Relaxation Delay	1.0000
10 Pulse Width	0.0000
11 Spectrometer Frequency	376.05
12 Spectral Width	89285.7
13 Lowest Frequency	-76739.2
14 Nucleus	19F
15 Acquired Size	65536
16 Spectral Size	131072

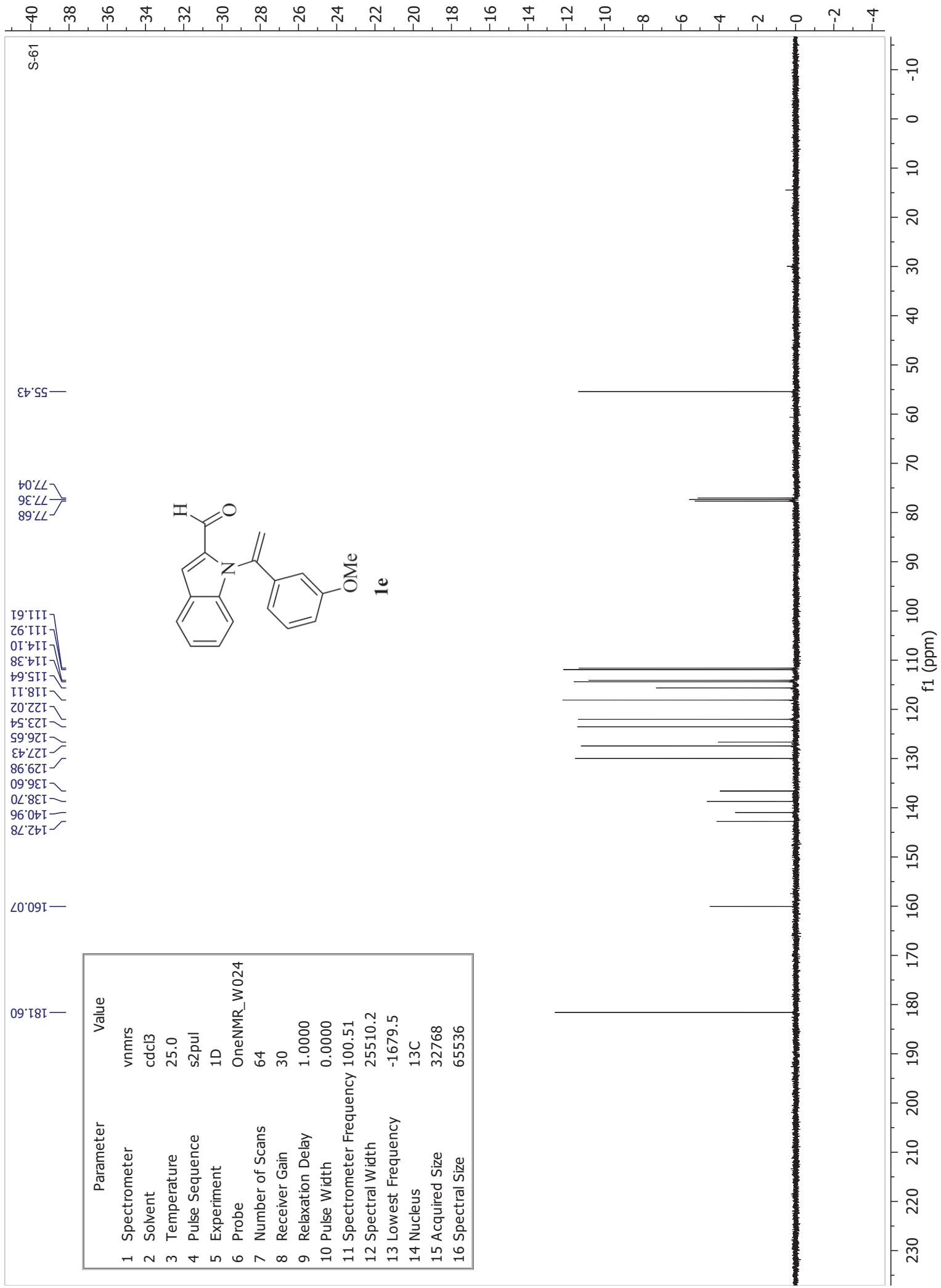
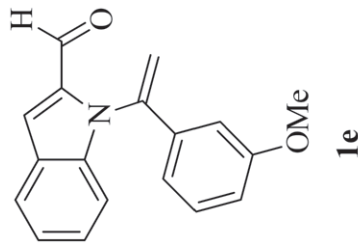


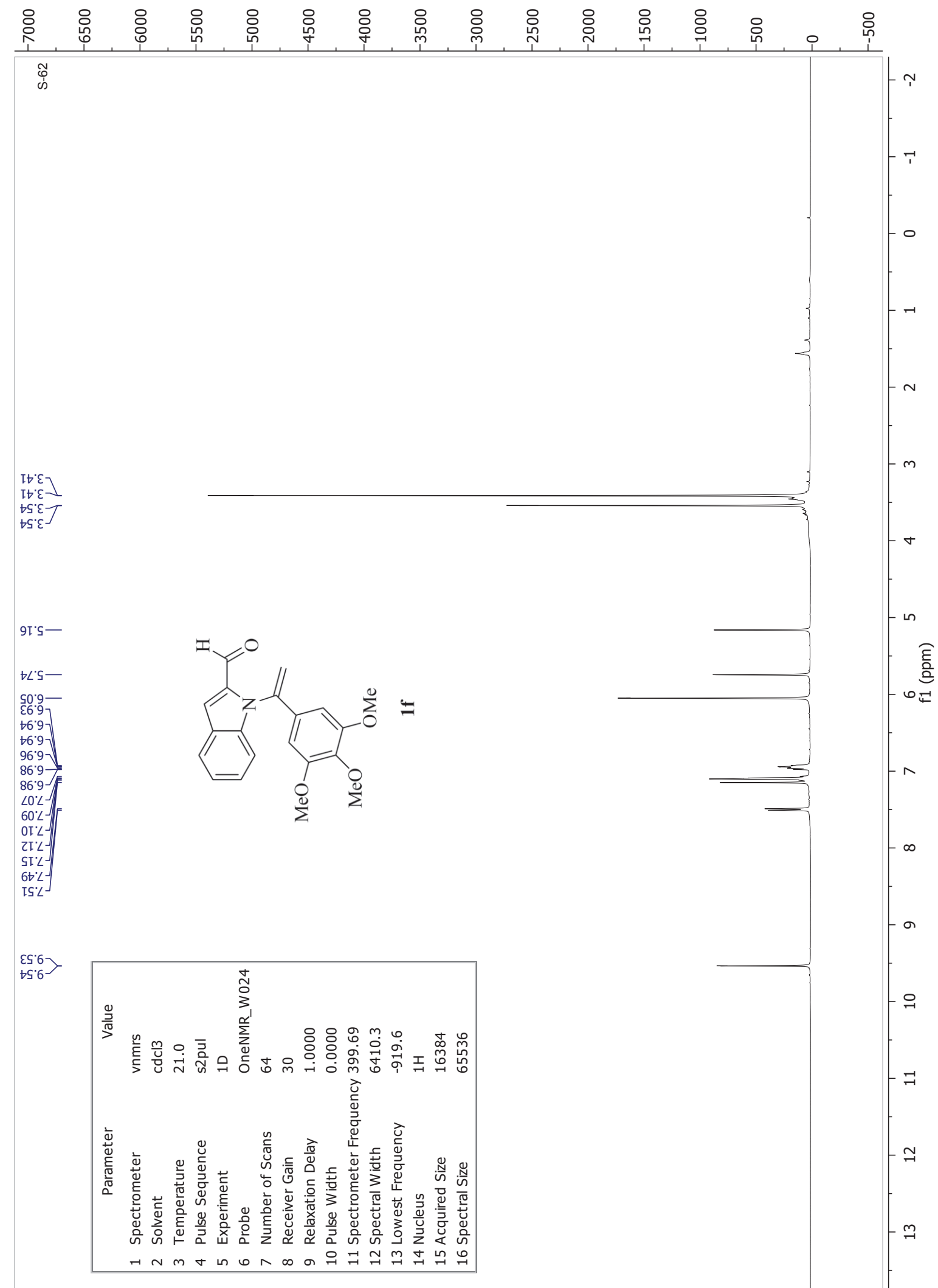
S-59

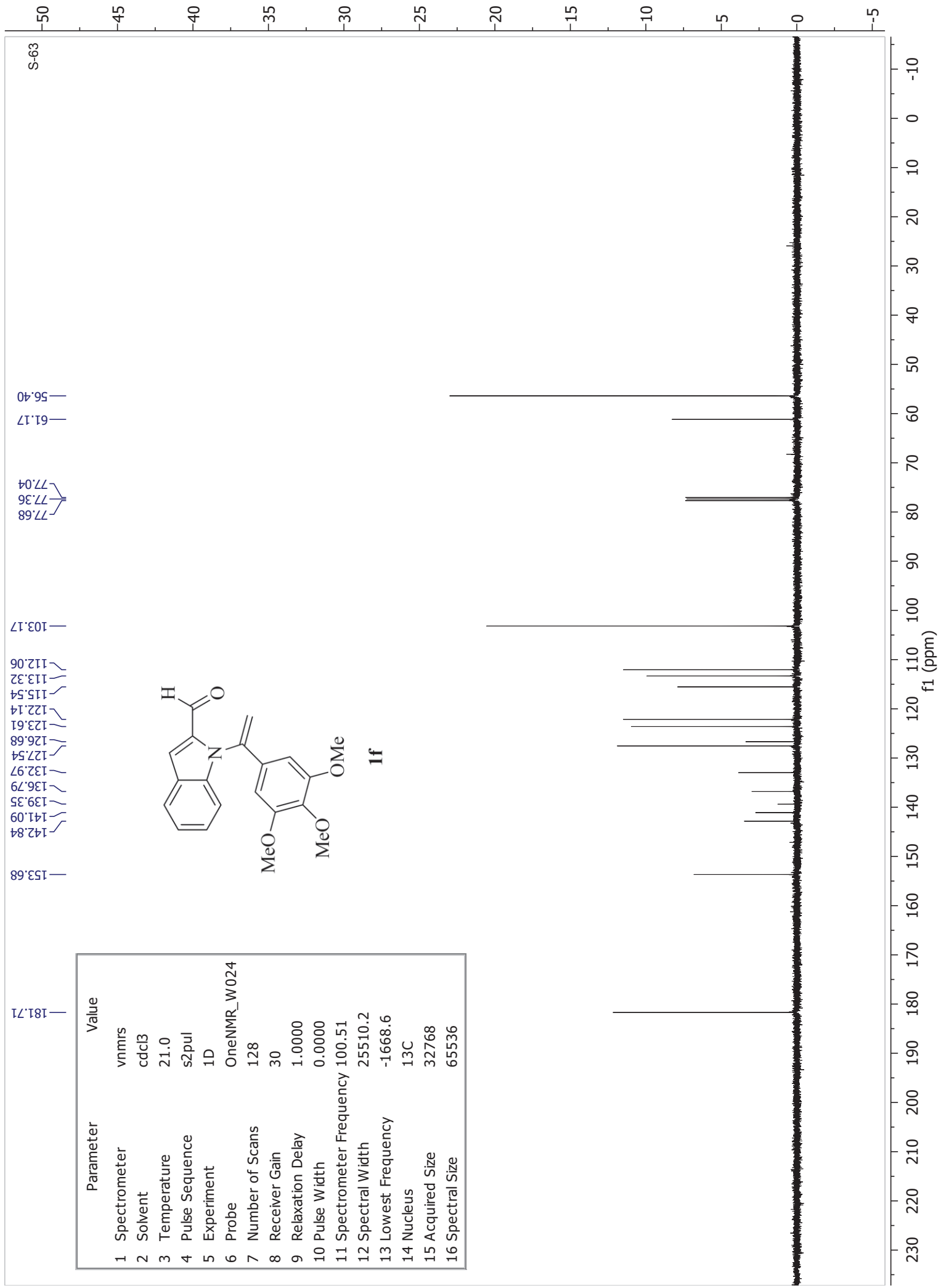
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

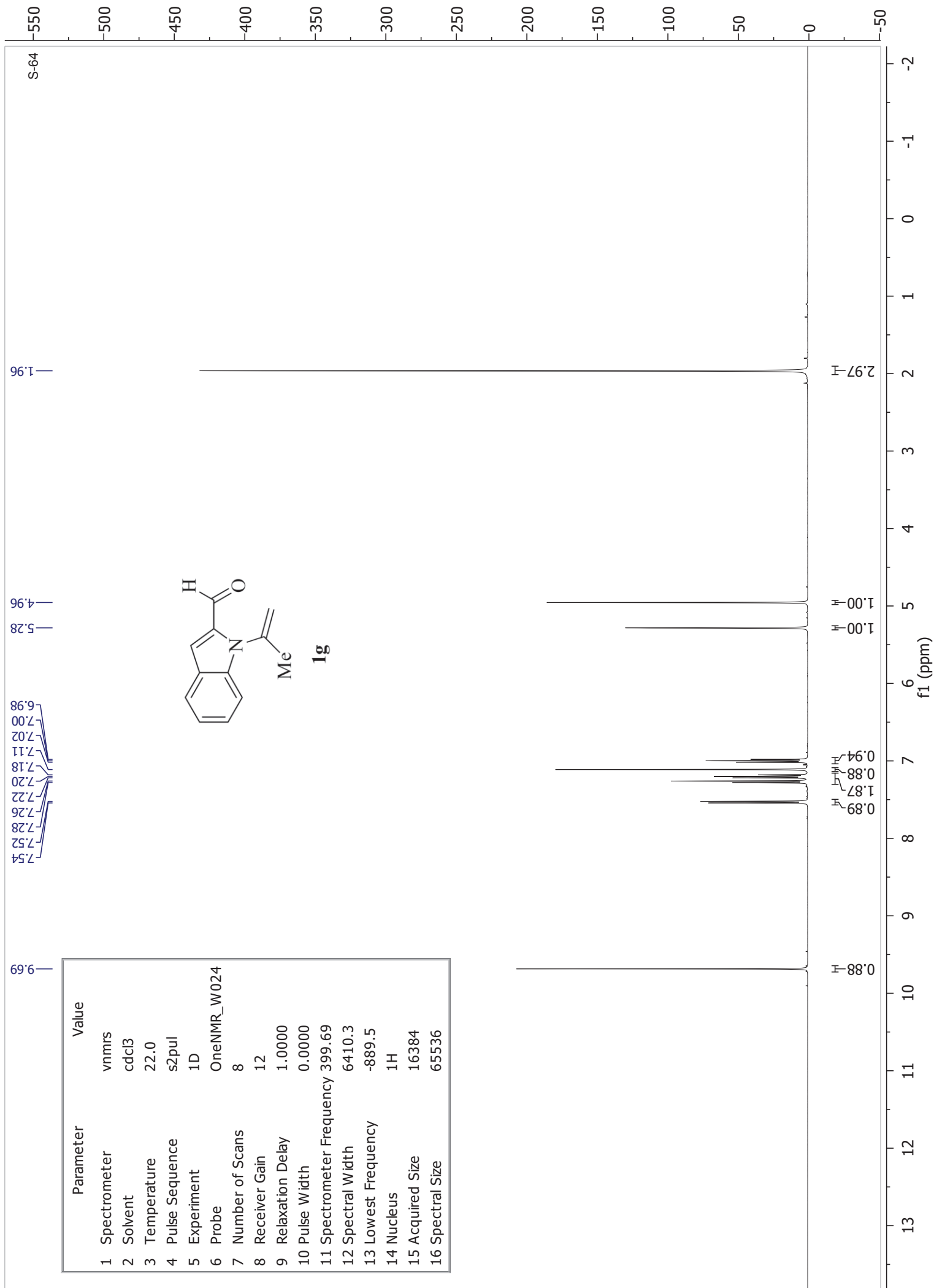


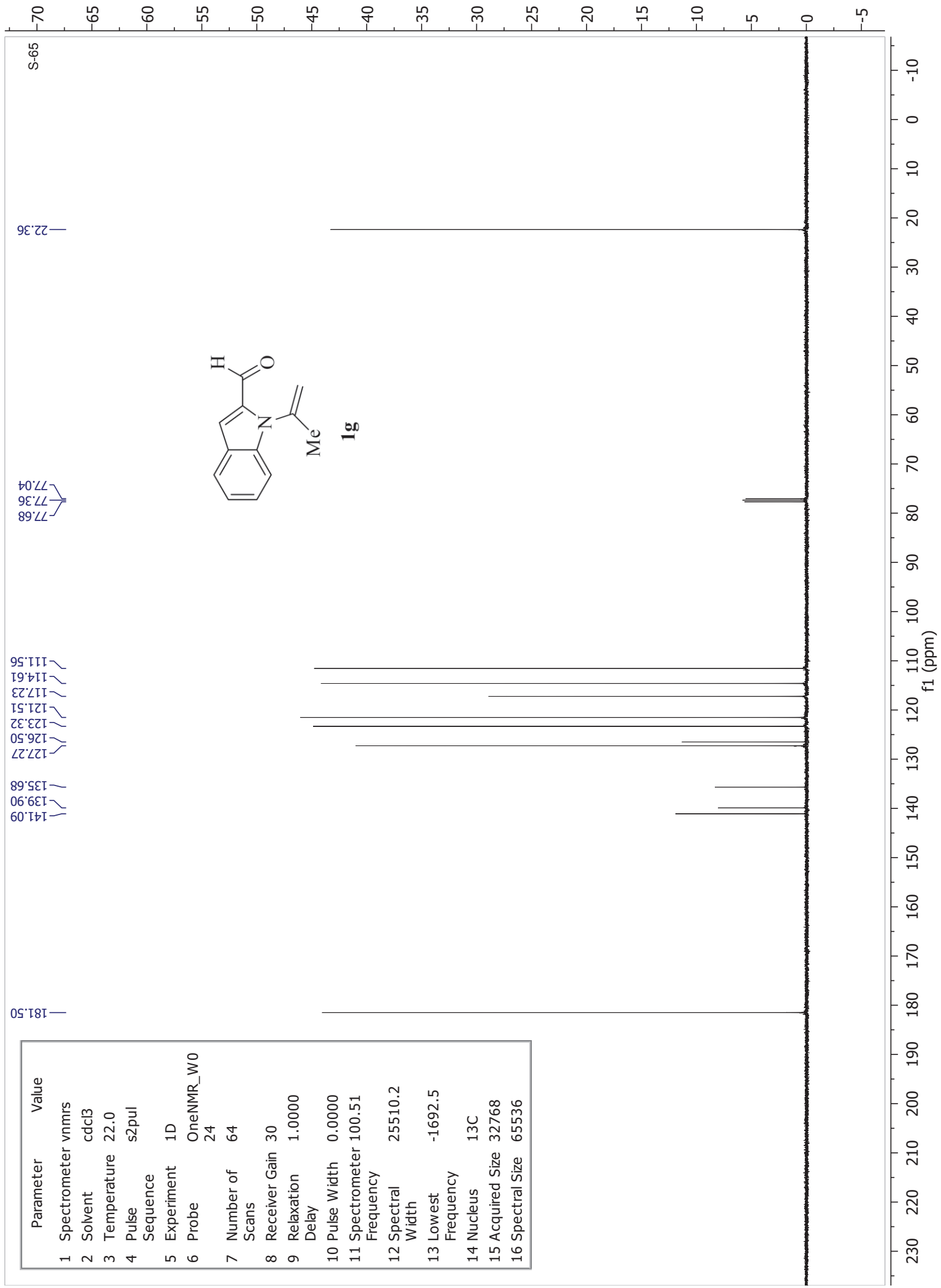
Parameter	Value
1 Spectrometer	nmrs
2 Solvent	cdcl3
3 Temperature	25.0
4 Pulse Sequence	s2pul
5 Experiment	1D
6 Probe	OneNMR_W024
7 Number of Scans	64
8 Receiver Gain	30
9 Relaxation Delay	1.0000
10 Pulse Width	0.0000
11 Spectrometer Frequency	100.51
12 Spectral Width	25510.2
13 Lowest Frequency	-1679.5
14 Nucleus	¹³ C
15 Acquired Size	32768
16 Spectral Size	65536

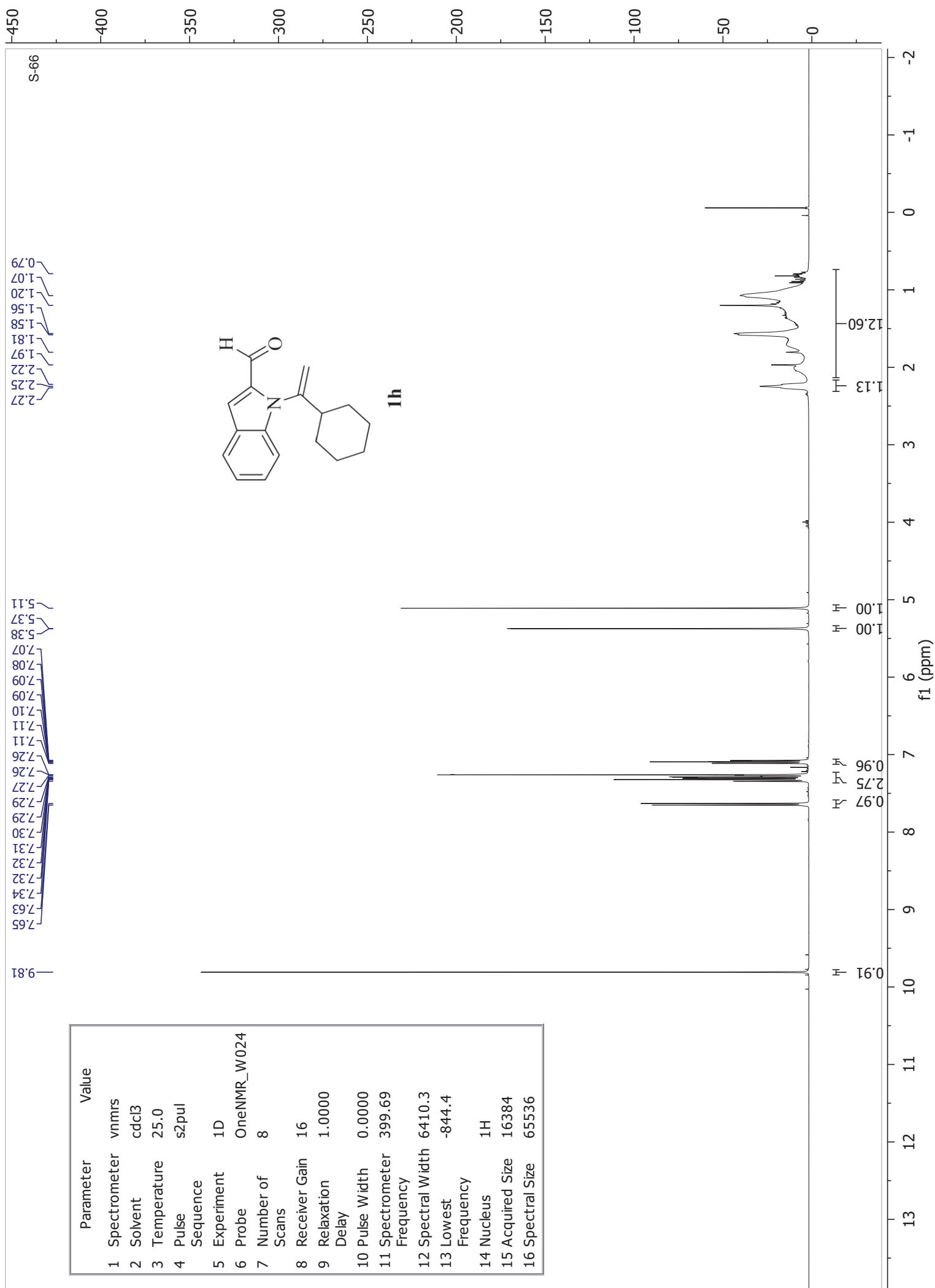




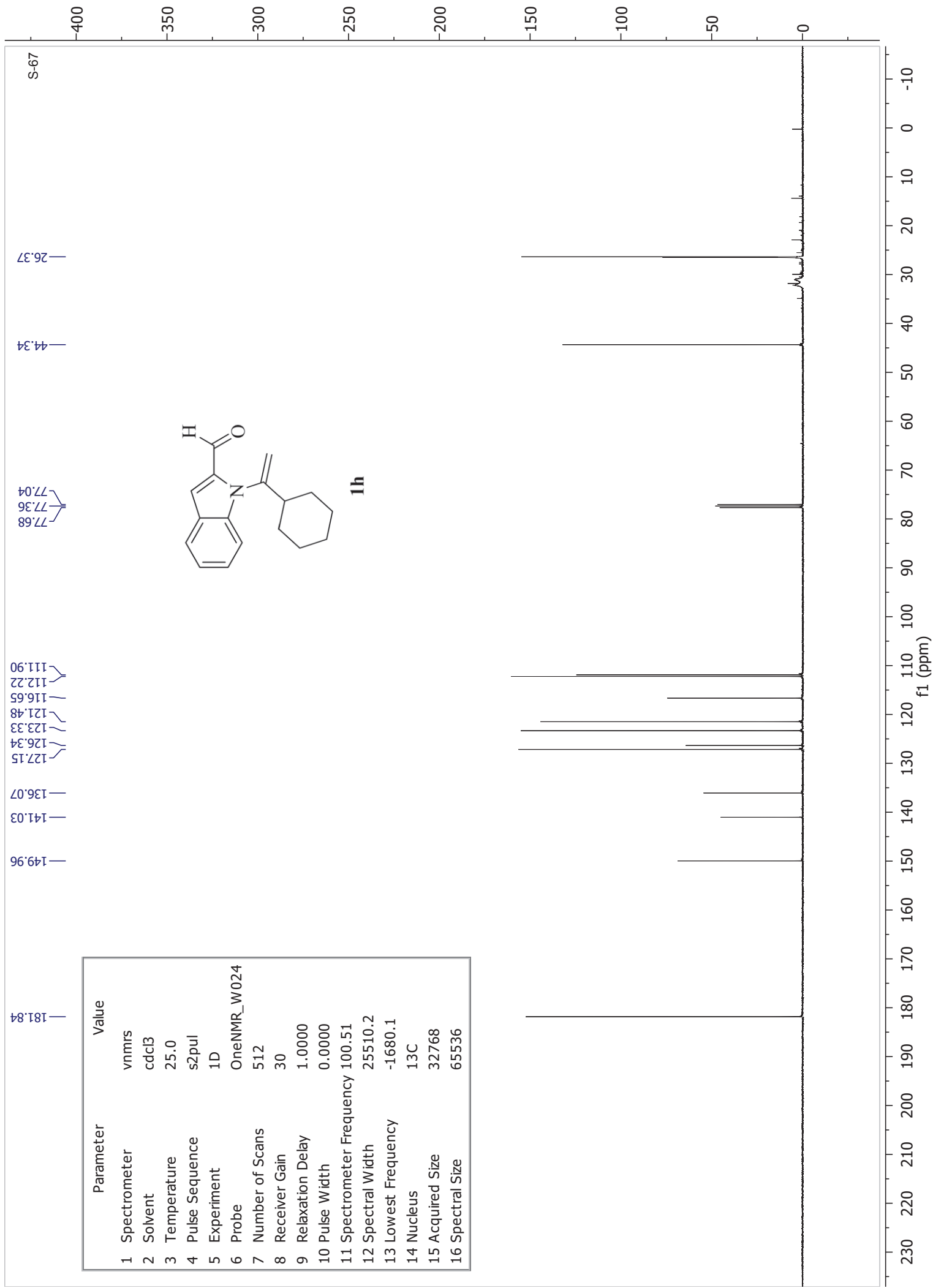
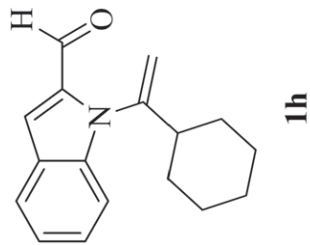


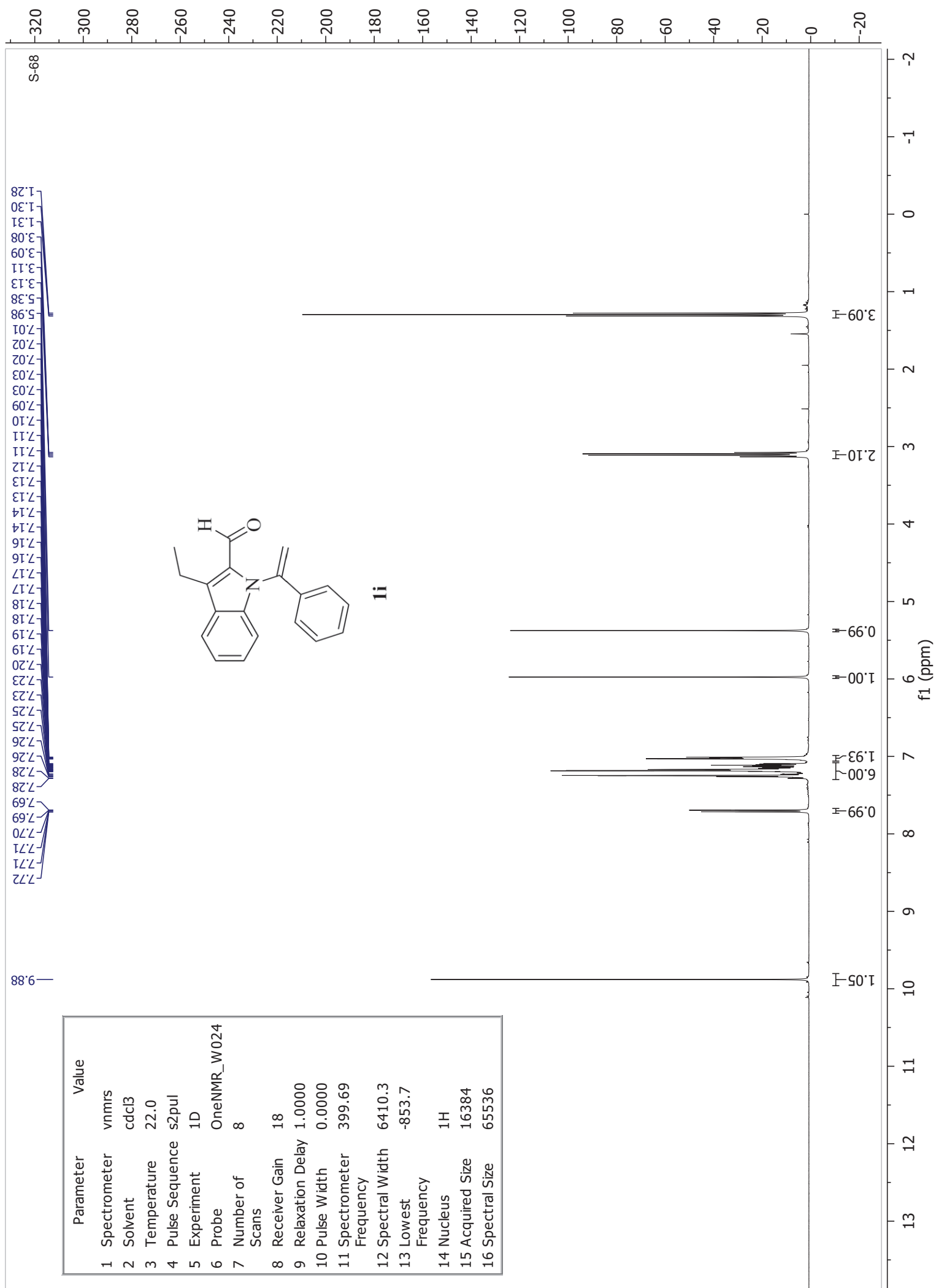


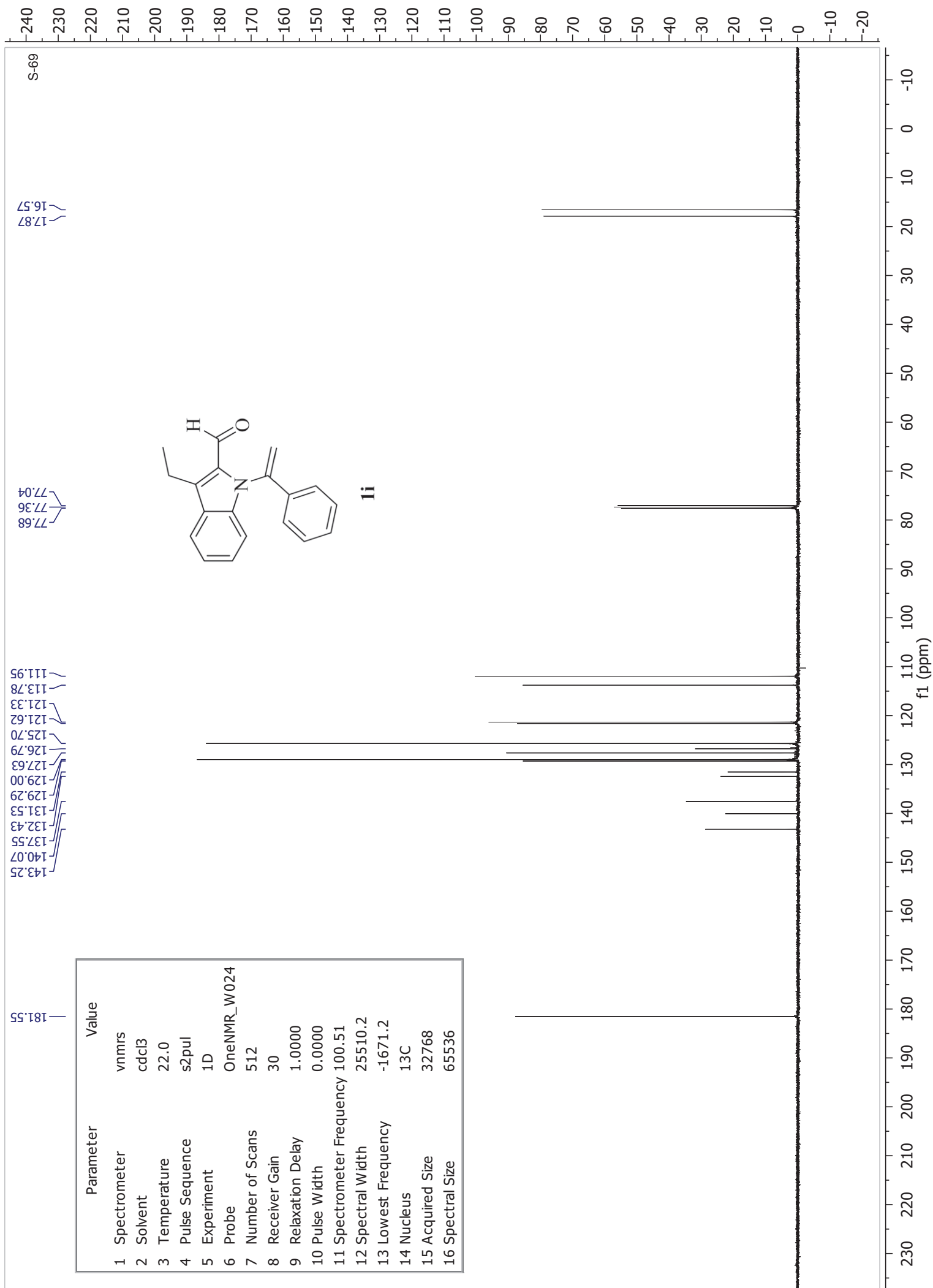


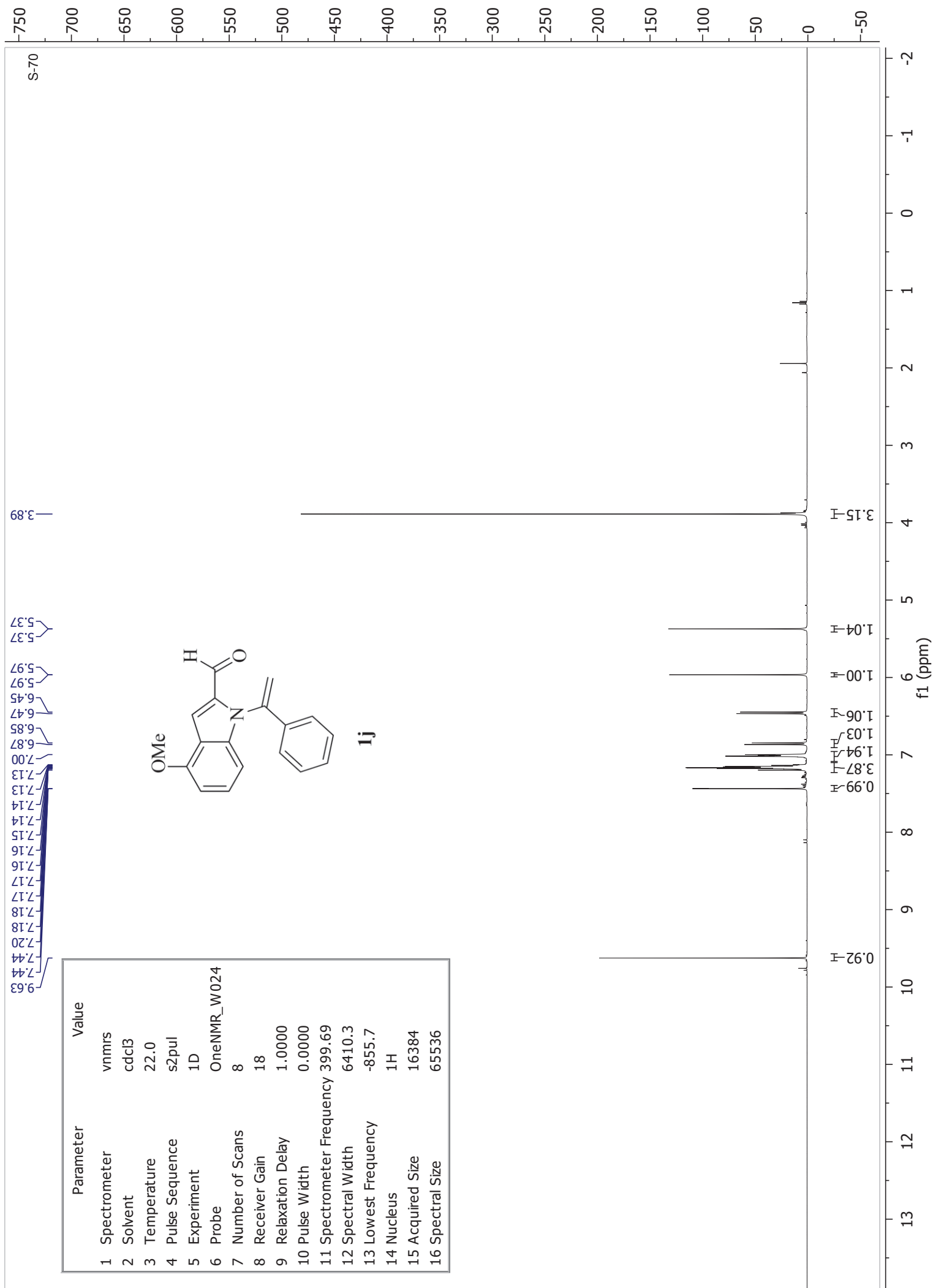


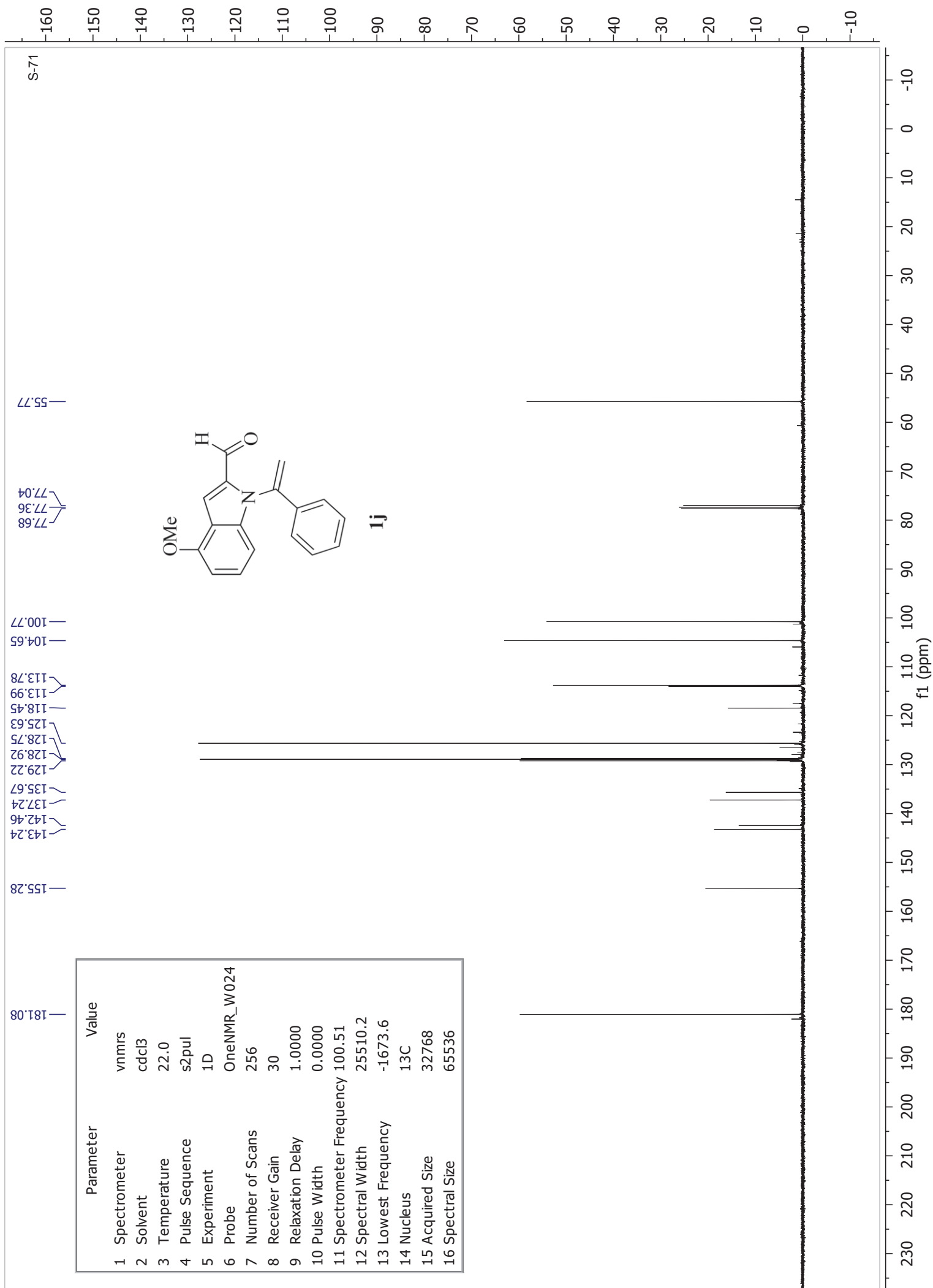
Parameter	Value
1 Spectrometer	nmrs
2 Solvent	cdcl3
3 Temperature	25.0
4 Pulse Sequence	s2pul
5 Experiment	1D
6 Probe	OneNMR_W024
7 Number of Scans	512
8 Receiver Gain	30
9 Relaxation Delay	1.0000
10 Pulse Width	0.0000
11 Spectrometer Frequency	100.51
12 Spectral Width	25510.2
13 Lowest Frequency	-1680.1
14 Nucleus	¹³ C
15 Acquired Size	32768
16 Spectral Size	65536

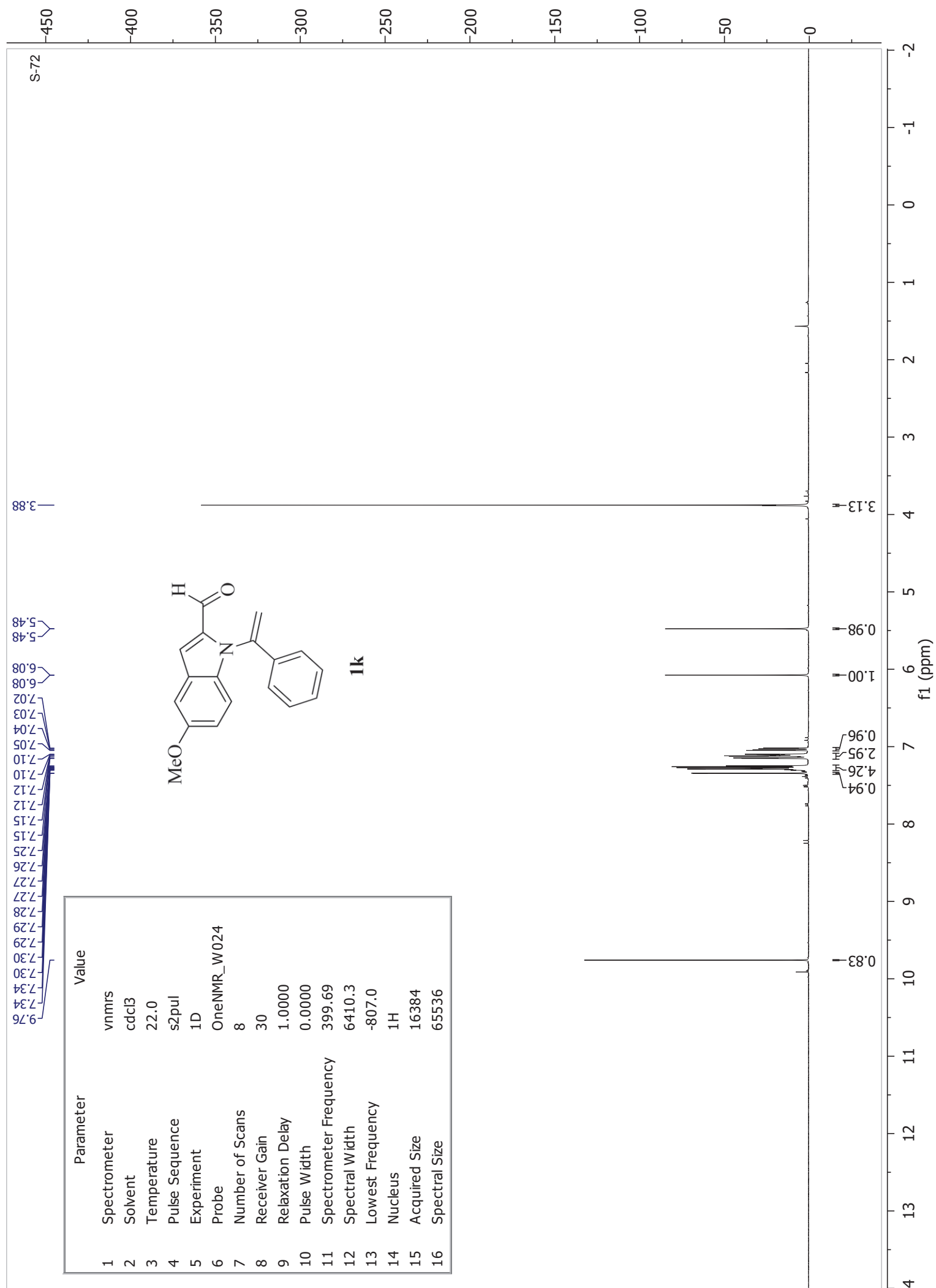


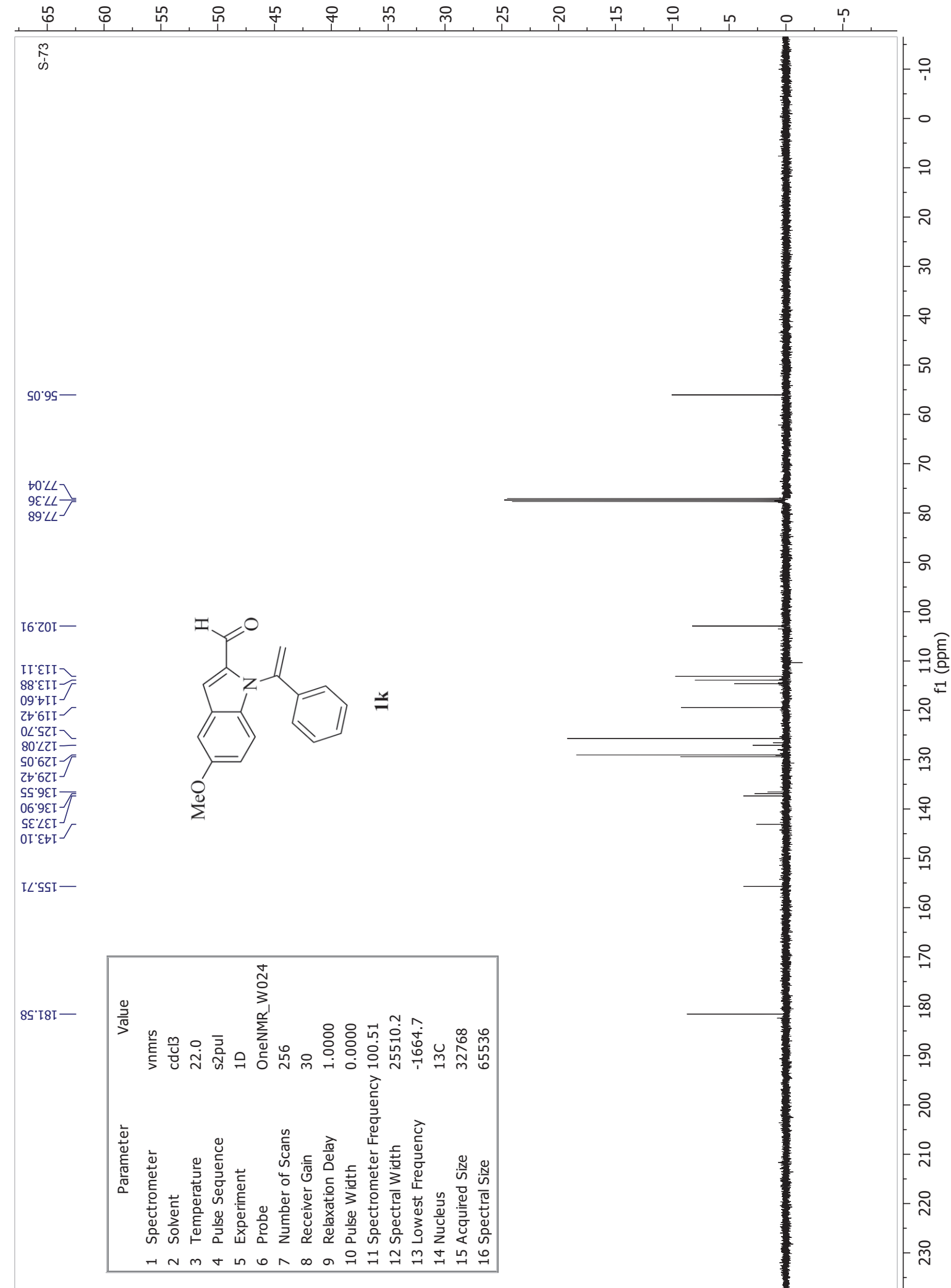


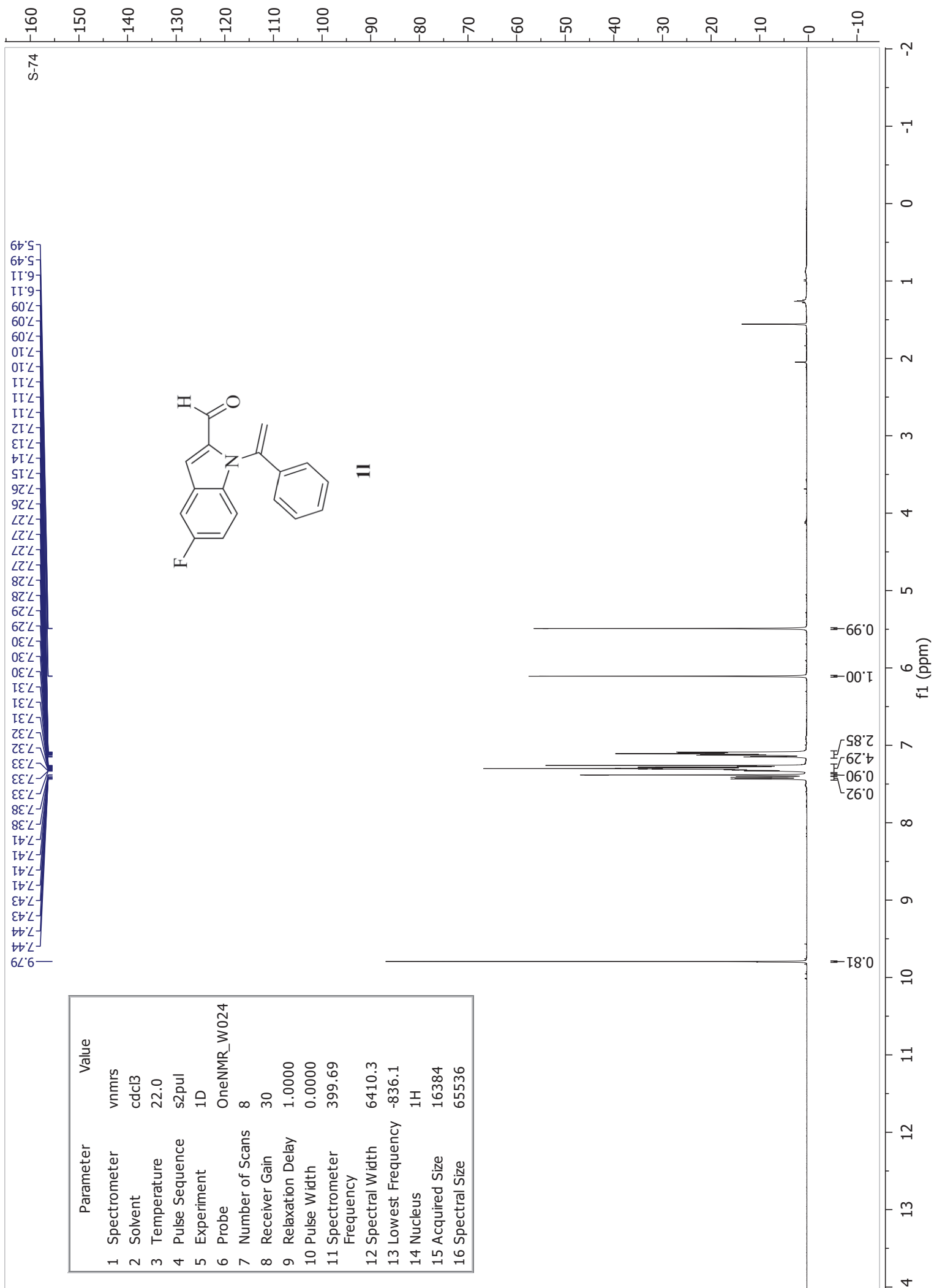


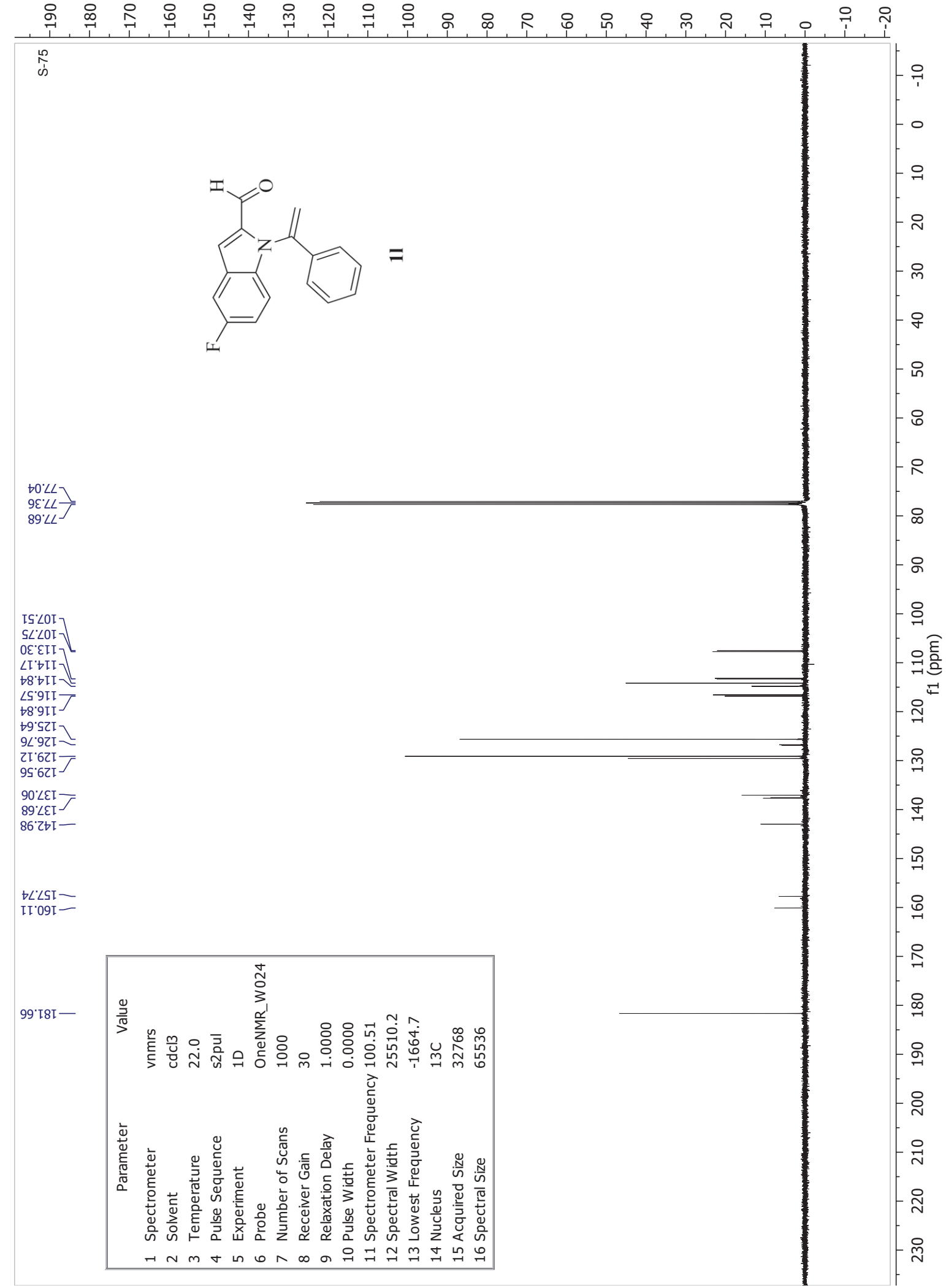


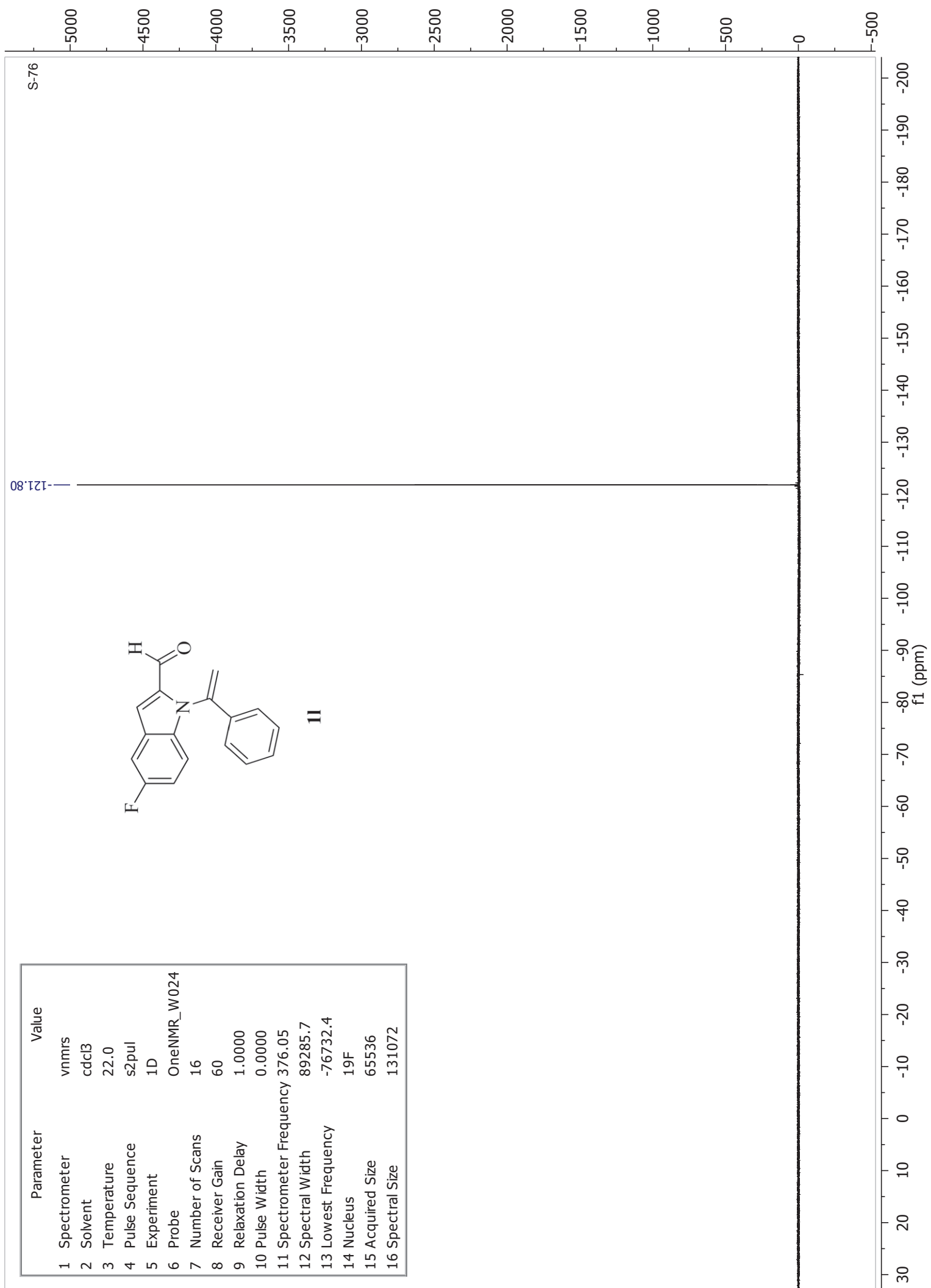


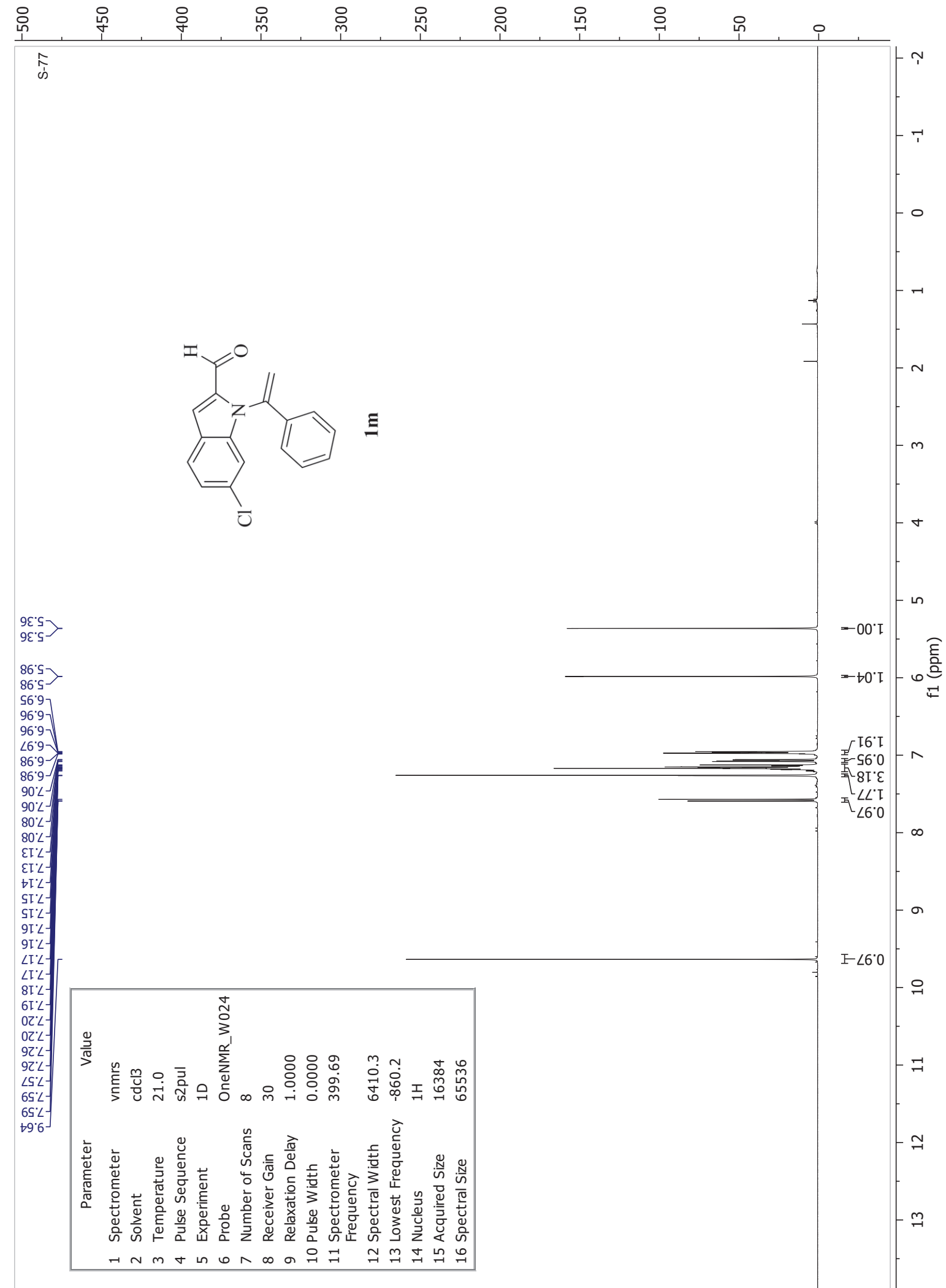


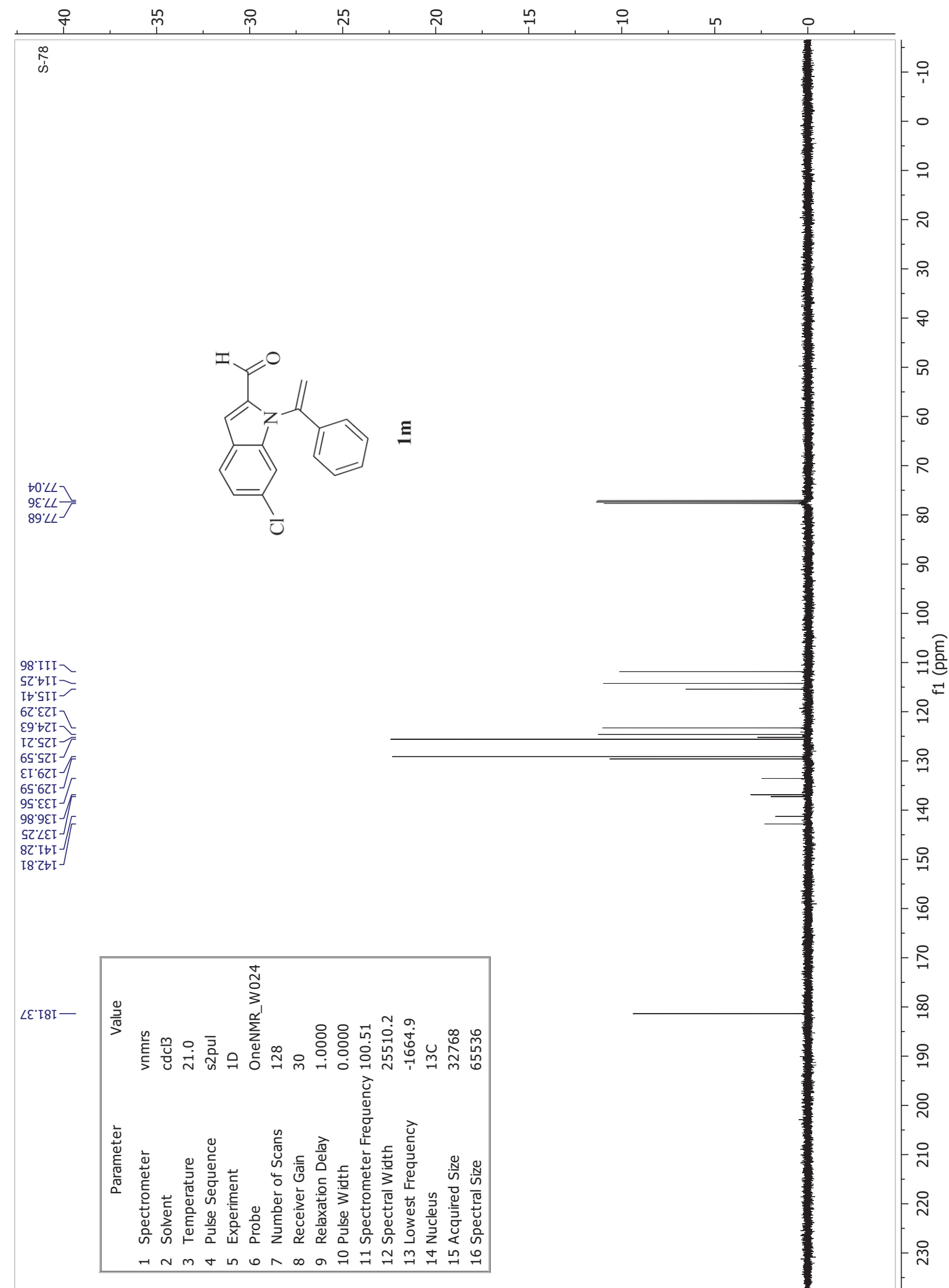


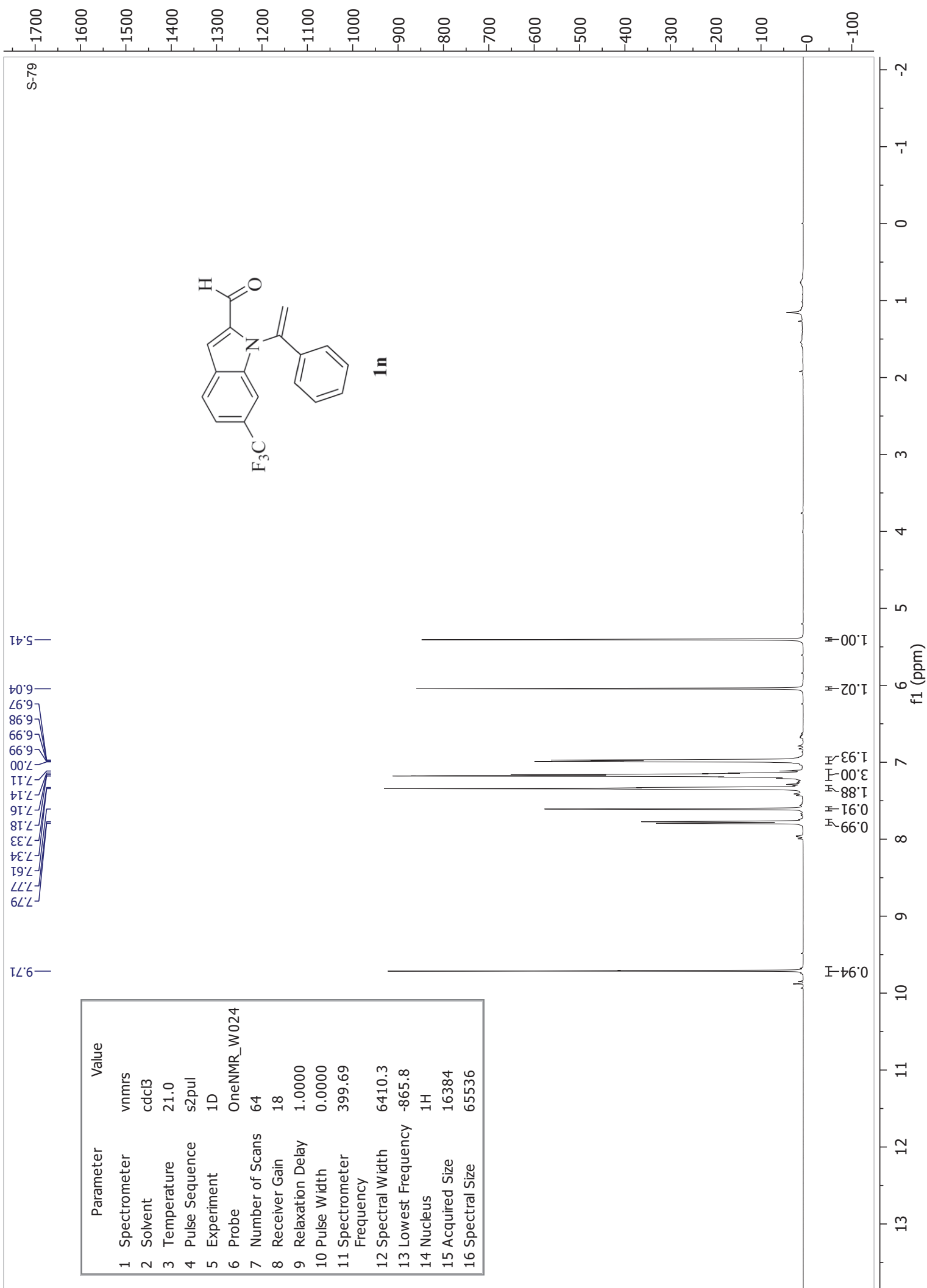






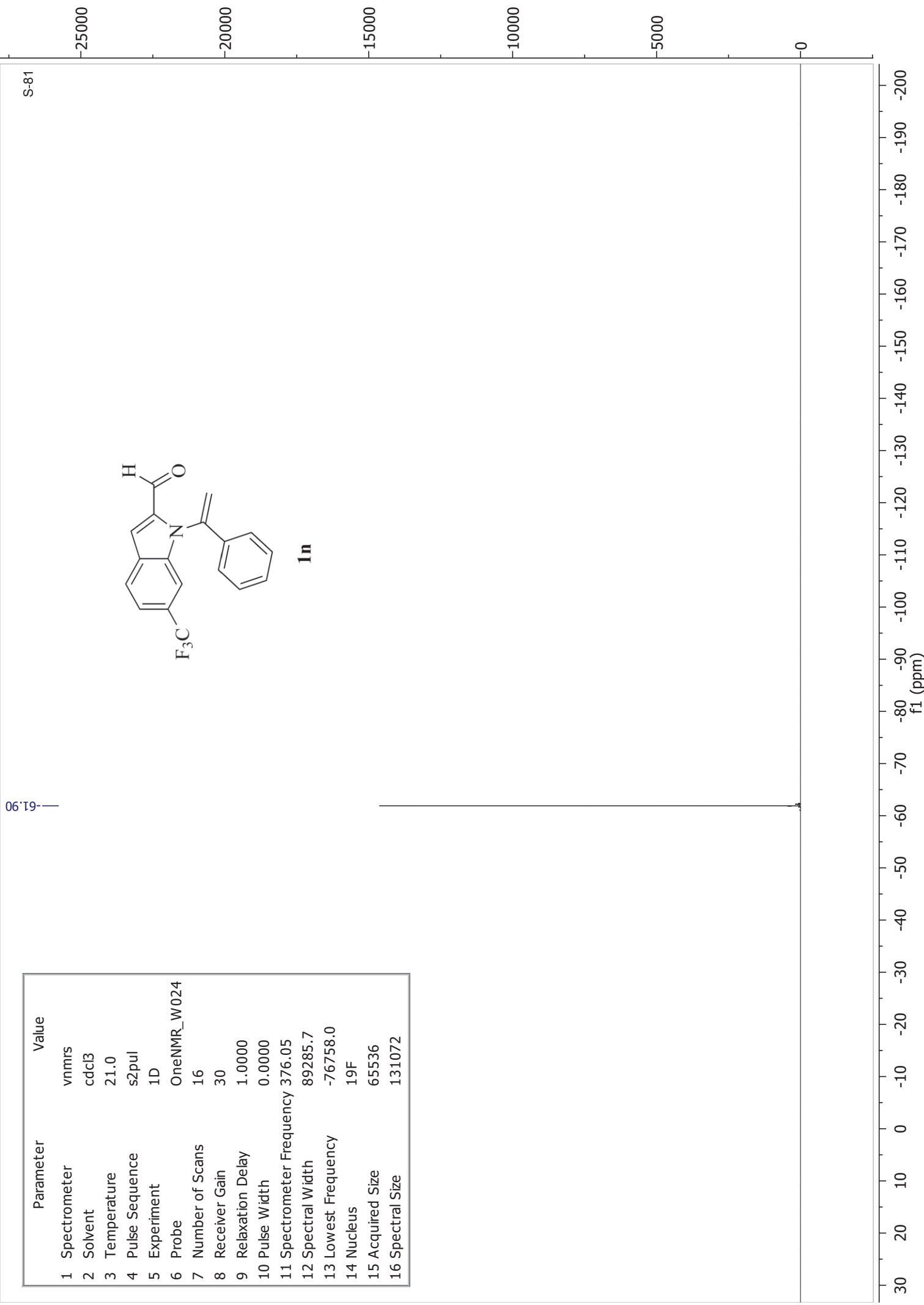


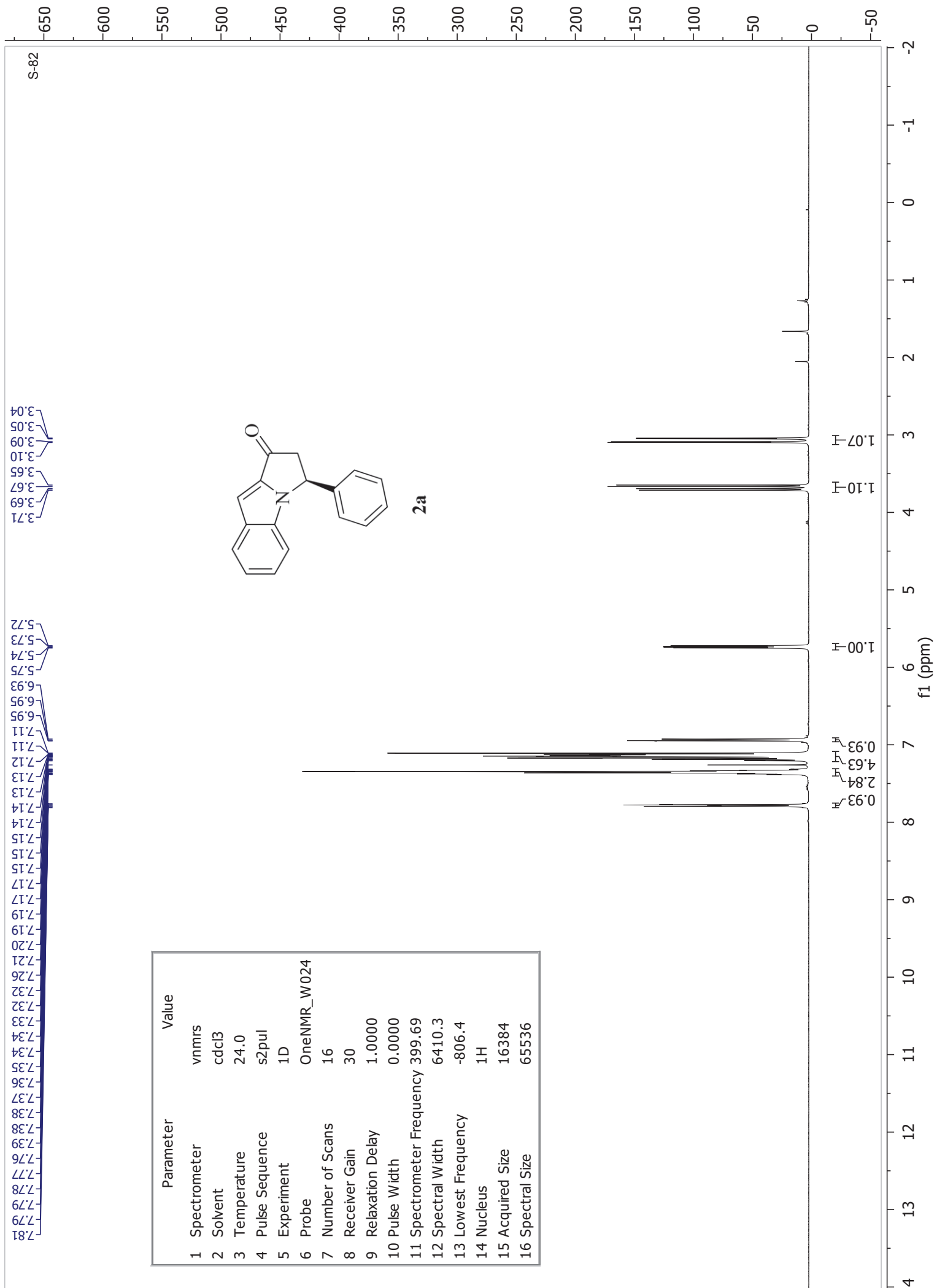


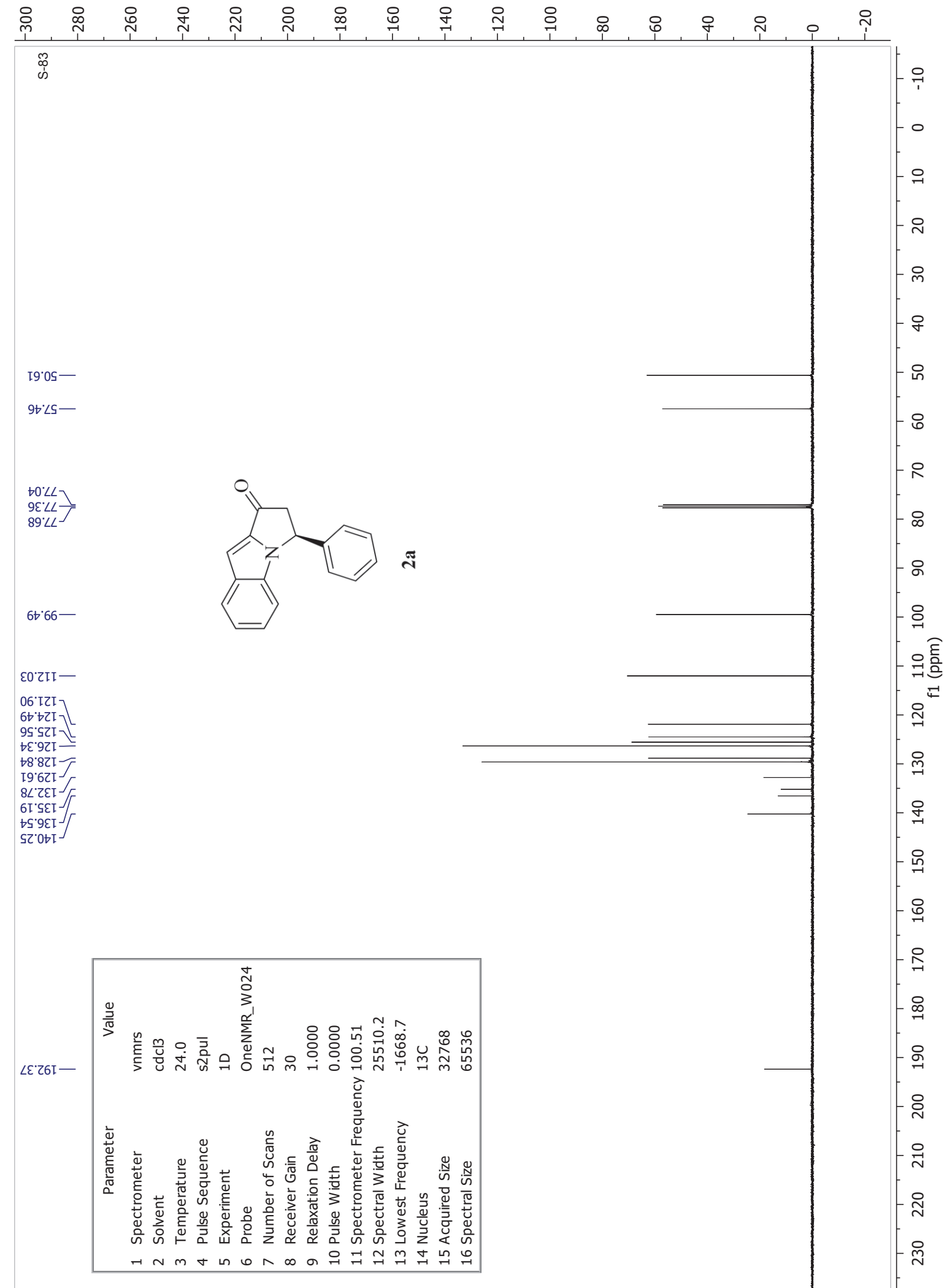


Parameter	Value
1 Spectrometer	nmrs
2 Solvent	cdcl3
3 Temperature	21.0
4 Pulse Sequence	s2pul
5 Experiment	1D
6 Probe	OneNMR_W024
7 Number of Scans	256
8 Receiver Gain	30
9 Relaxation Delay	1.0000
10 Pulse Width	0.0000
11 Spectrometer Frequency	100.51
12 Spectral Width	25510.2
13 Lowest Frequency	-1672.0
14 Nucleus	¹³ C
15 Acquired Size	32768
16 Spectral Size	65536







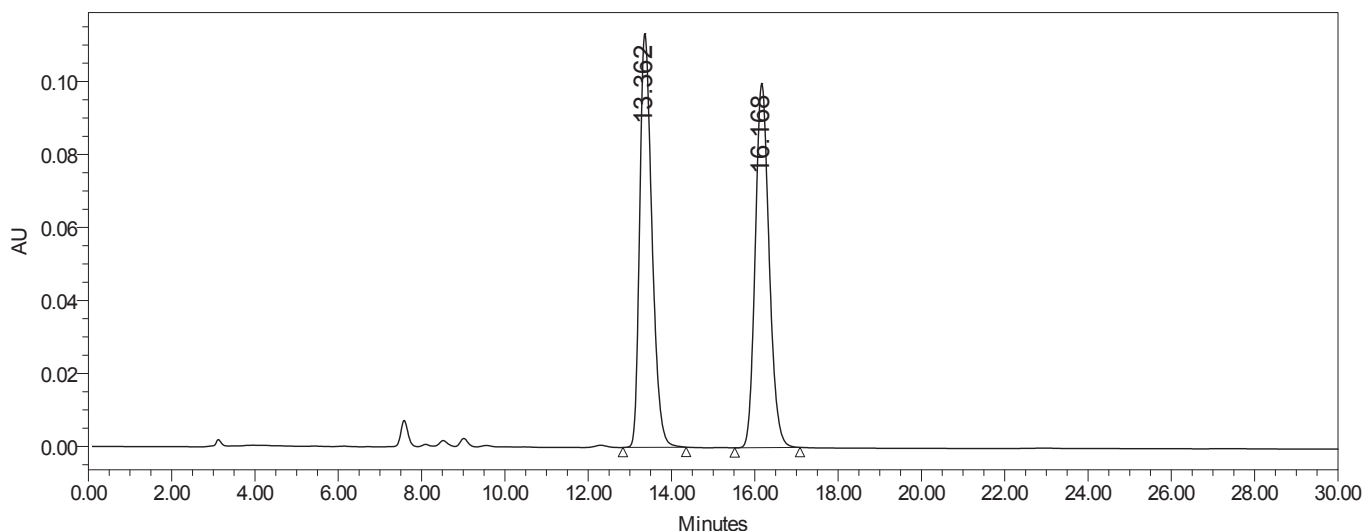




Injection Summary Report

SAMPLE INFORMATION

Sample Name:	AG_70_F1_5%IPA_ADH_1mpm	Acquired By:	System
Sample Type:	Unknown	Sample Set Name	
Vial:	61	Acq. Method Set:	1_ADH 95_5 1mpm
Injection #:	1	Processing Method	70
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	30.0 Minutes	Proc. Chnl. Descr.:	W2489 ChA 254nm
Date Acquired:	6/15/2012 2:00:56 PM CDT		
Date Processed:	9/25/2013 2:53:00 PM CDT		



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 6889; Processing Method: 70

Processed Channel Descr.: W2489 ChA 254nm

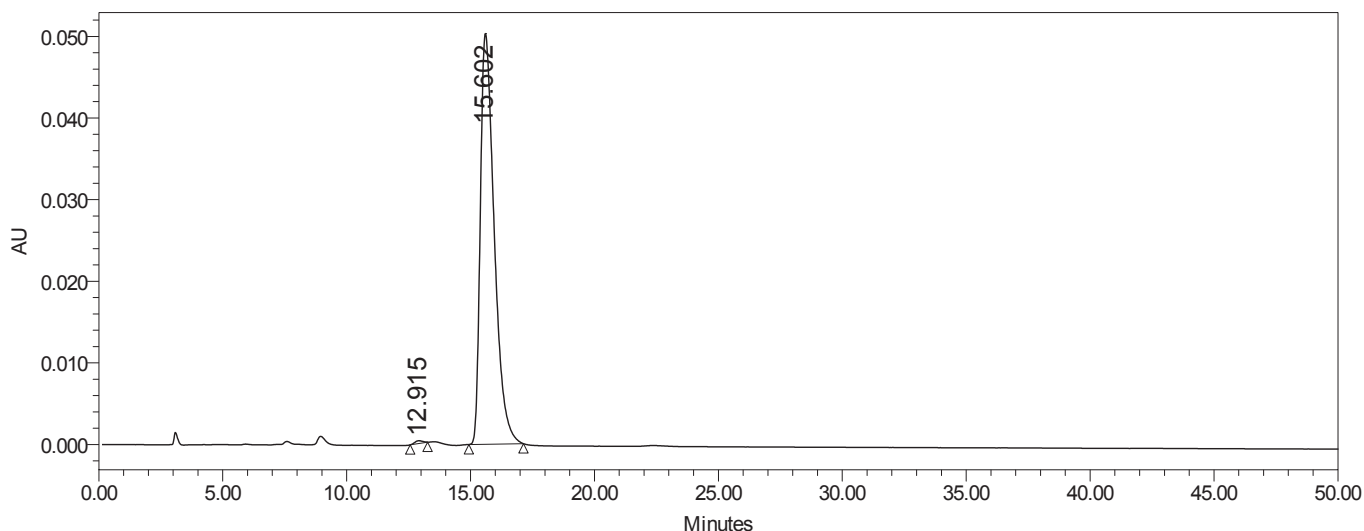
	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	13.362	2319785	50.08	113477
2	W2489 ChA 254nm	16.168	2312330	49.92	99850



Injection Summary Report

SAMPLE INFORMATION

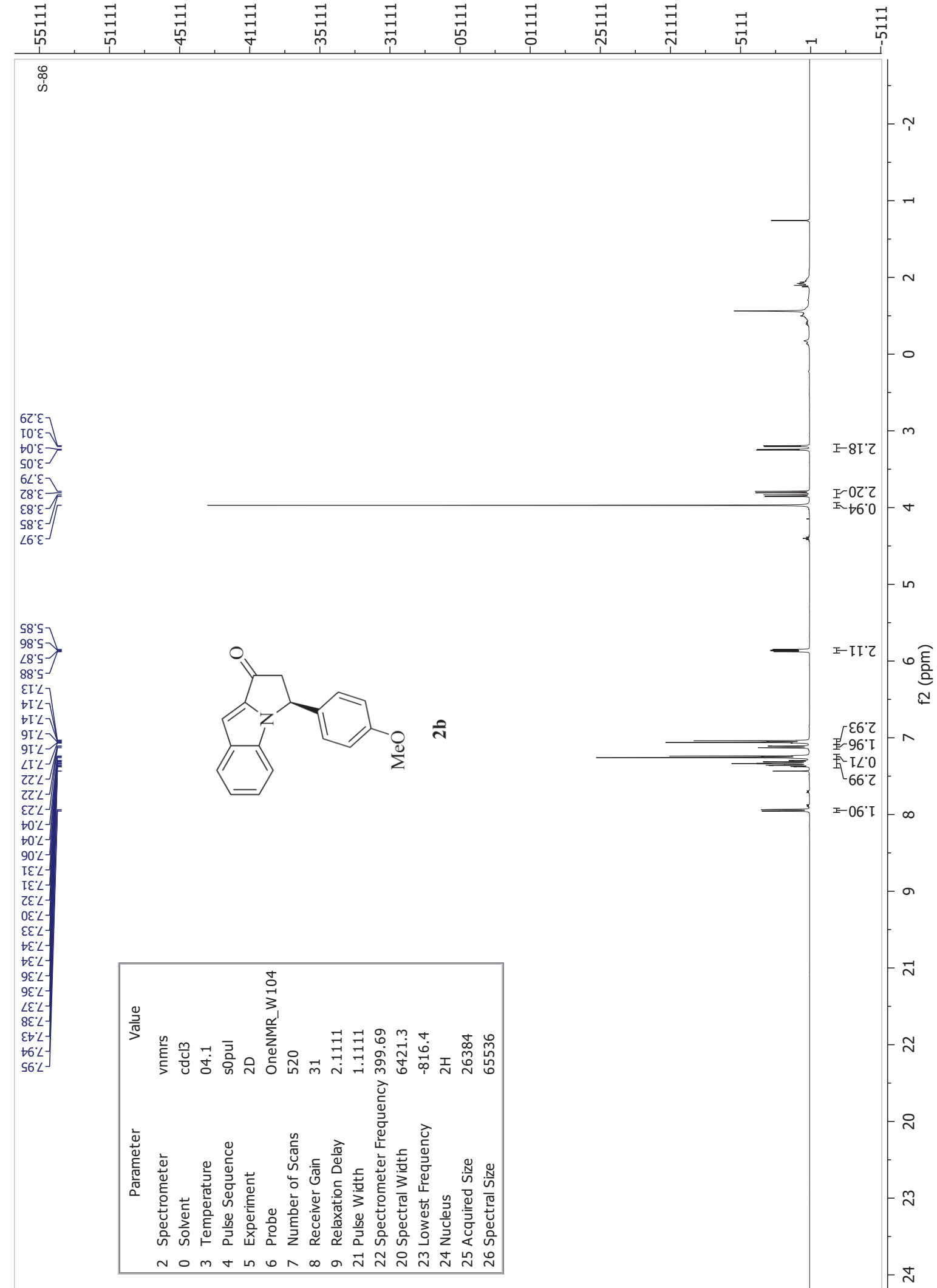
Sample Name:		Acquired By:	System
Sample Type:	Unknown	Sample Set Name	Megan2
Vial:	20	Acq. Method Set:	1_ADH 95_5 1mpm
Injection #:	1	Processing Method	132
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	50.0 Minutes	Proc. Chnl. Descr.:	W2489 ChA 254nm
Date Acquired:	7/29/2013 7:40:50 PM CDT		
Date Processed:	9/25/2013 2:46:35 PM CDT		

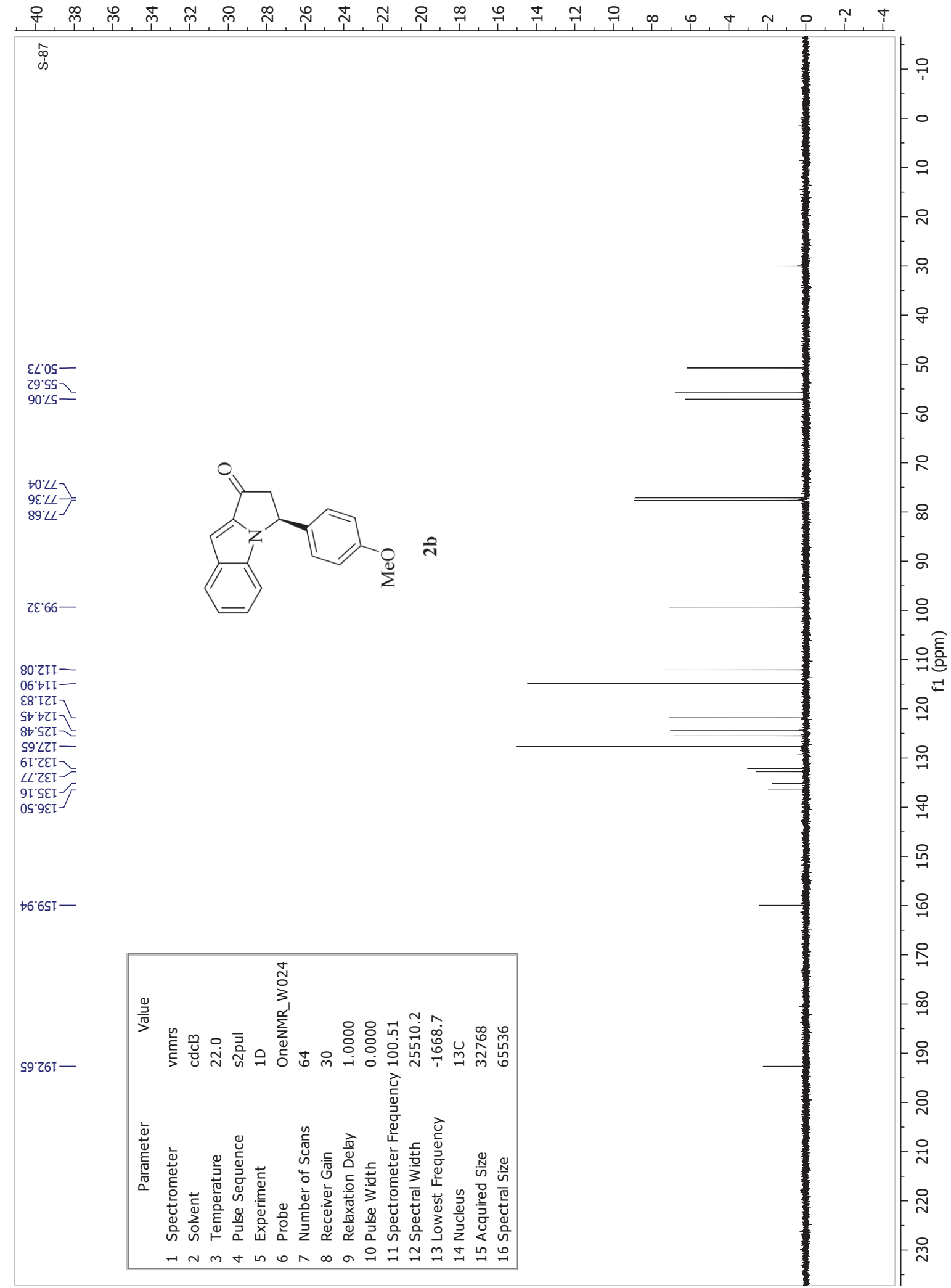


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 6885; Processing Method: 132

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	12.915	7504	0.38	343
2	W2489 ChA 254nm	15.602	1954517	99.62	50325



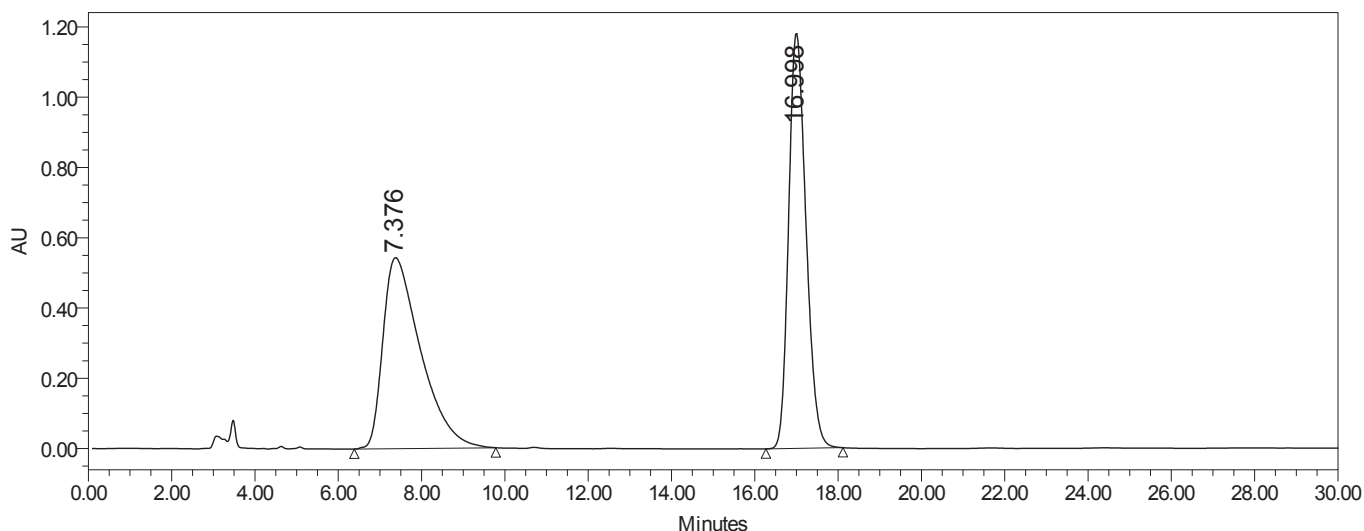




Injection Summary Report

SAMPLE INFORMATION

Sample Name:		Acquired By:	System
Sample Type:	Unknown	Sample Set Name	
Vial:	10	Acq. Method Set:	3_ODH 90_10 1mpm
Injection #:	1	Processing Method	130
Injection Volume:	10.00 ul	Channel Name:	W2489 ChB
Run Time:	30.0 Minutes	Proc. Chnl. Descr.:	W2489 ChB 220nm
Date Acquired:	9/5/2012 3:46:45 PM CDT		
Date Processed:	9/24/2013 9:55:34 PM CDT		



Channel: W2489 ChB; Processed Channel: W2489 ChB 220nm; Result Id: 6801; Processing Method: 130

Processed Channel Descr.: W2489 ChB 220nm

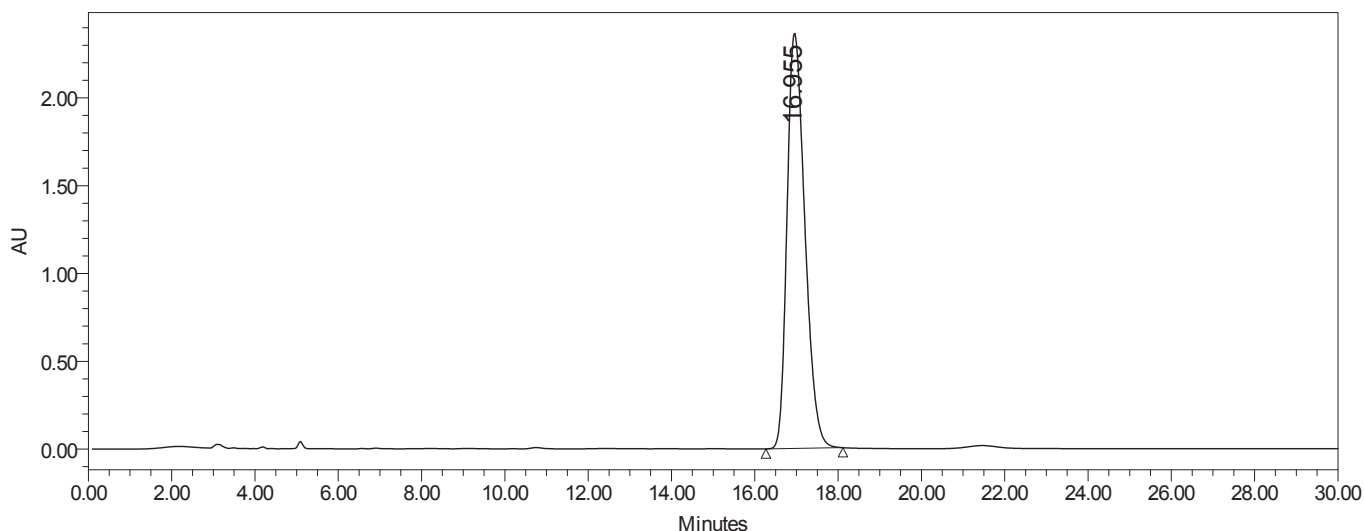
	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 220nm	7.376	34160557	50.00	543264
2	W2489 ChB 220nm	16.998	34161609	50.00	1180830



Injection Summary Report

SAMPLE INFORMATION

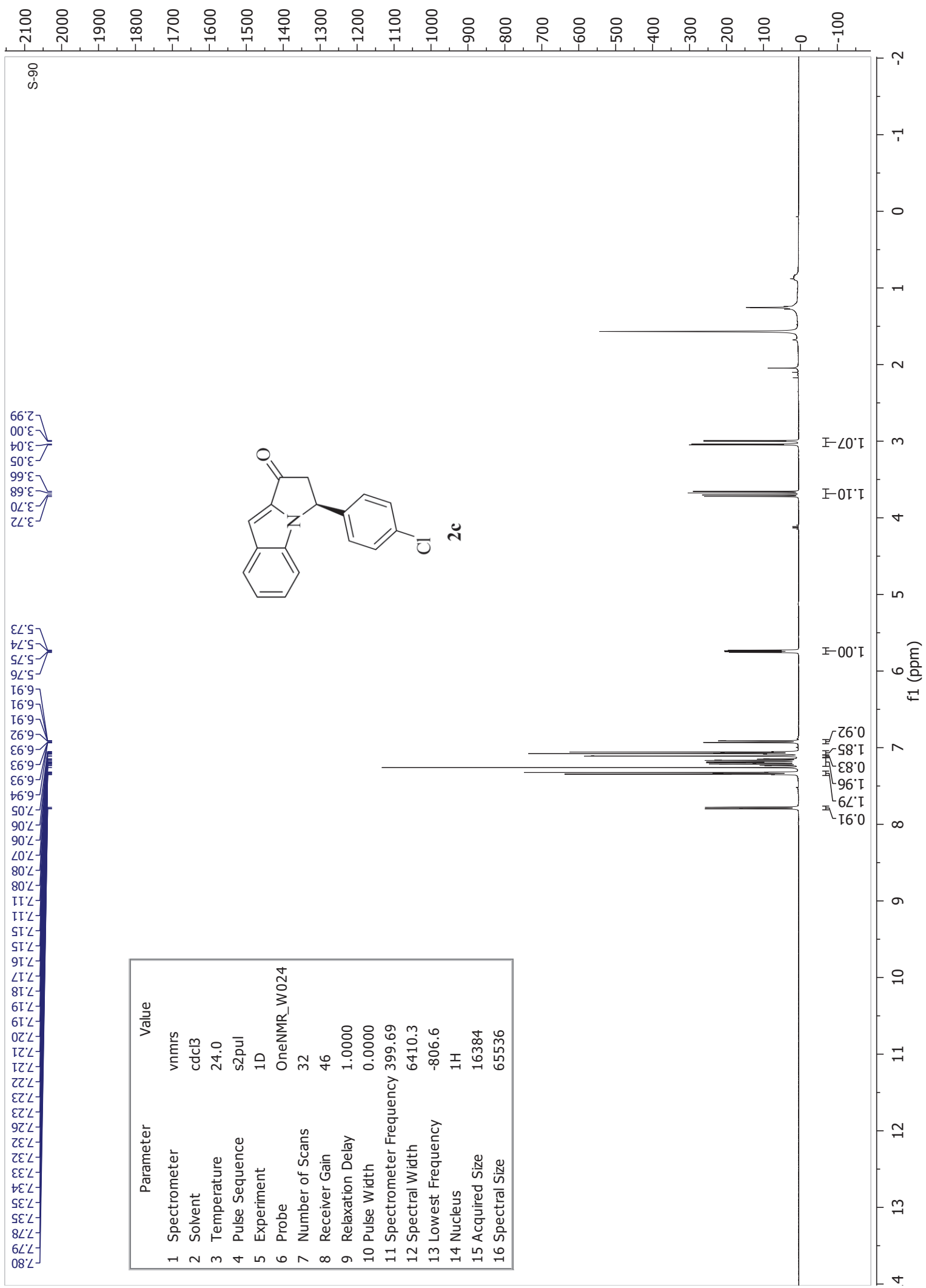
Sample Name:		Acquired By:	System
Sample Type:	Unknown	Sample Set Name	
Vial:	11	Acq. Method Set:	3_ODH 90_10 1mpm
Injection #:	1	Processing Method	128
Injection Volume:	10.00 ul	Channel Name:	W2489 ChB
Run Time:	30.0 Minutes	Proc. Chnl. Descr.:	W2489 ChB 220nm
Date Acquired:	9/5/2012 5:10:24 PM CDT		
Date Processed:	9/24/2013 9:57:35 PM CDT		



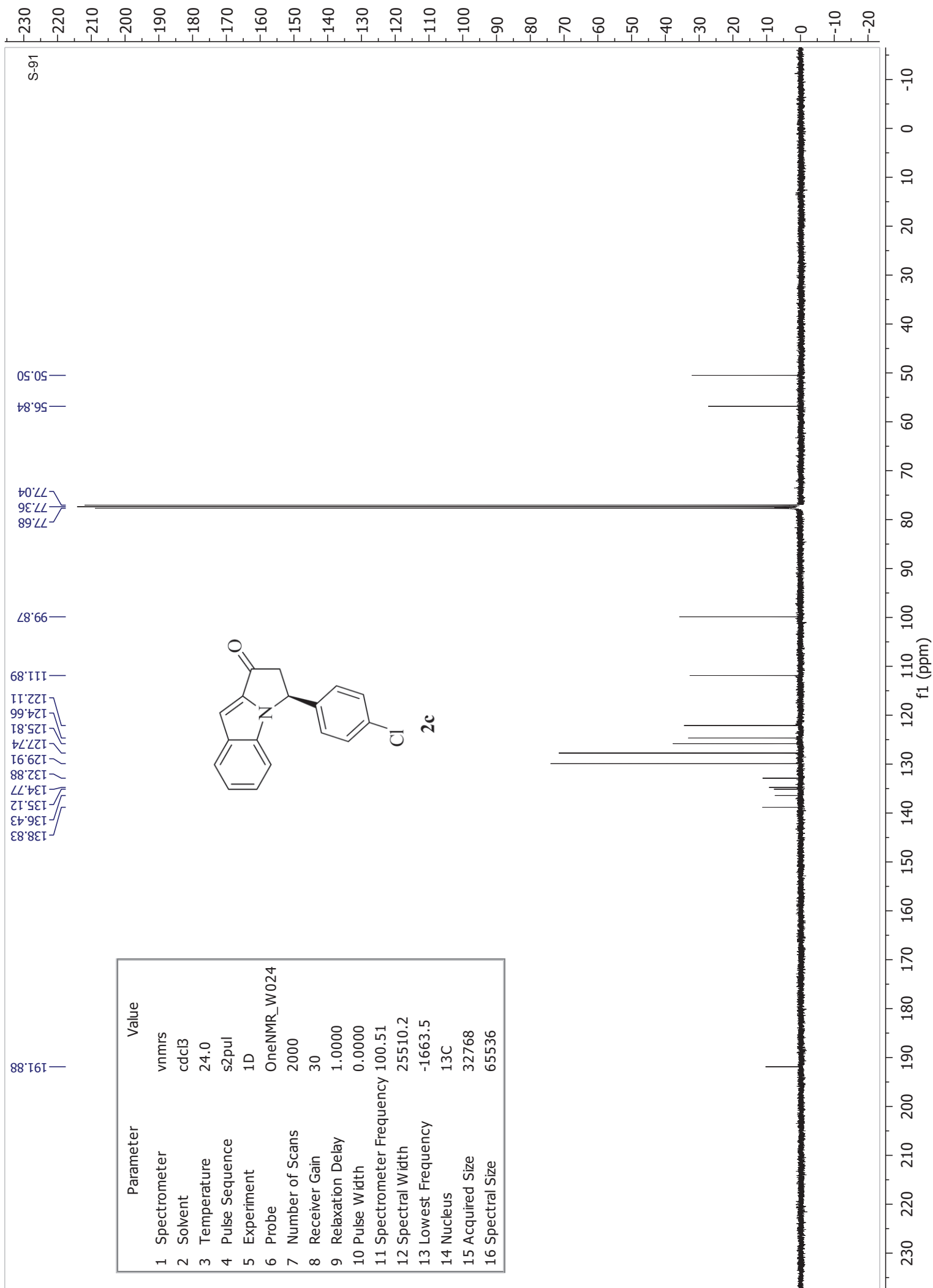
Channel: W2489 ChB; Processed Channel: W2489 ChB 220nm; Result Id: 6803; Processing Method: 128

Processed Channel Descr.: W2489 ChB 220nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 220nm	16.955	70231477	100.00	2363863



Parameter	Value
1 Spectrometer	nmrs
2 Solvent	cdcl3
3 Temperature	24.0
4 Pulse Sequence	s2pul
5 Experiment	1D
6 Probe	OneNMR_W024
7 Number of Scans	32
8 Receiver Gain	46
9 Relaxation Delay	1.0000
10 Pulse Width	0.0000
11 Spectrometer Frequency	399.69
12 Spectral Width	6410.3
13 Lowest Frequency	-806.6
14 Nucleus	1H
15 Acquired Size	16384
16 Spectral Size	65536

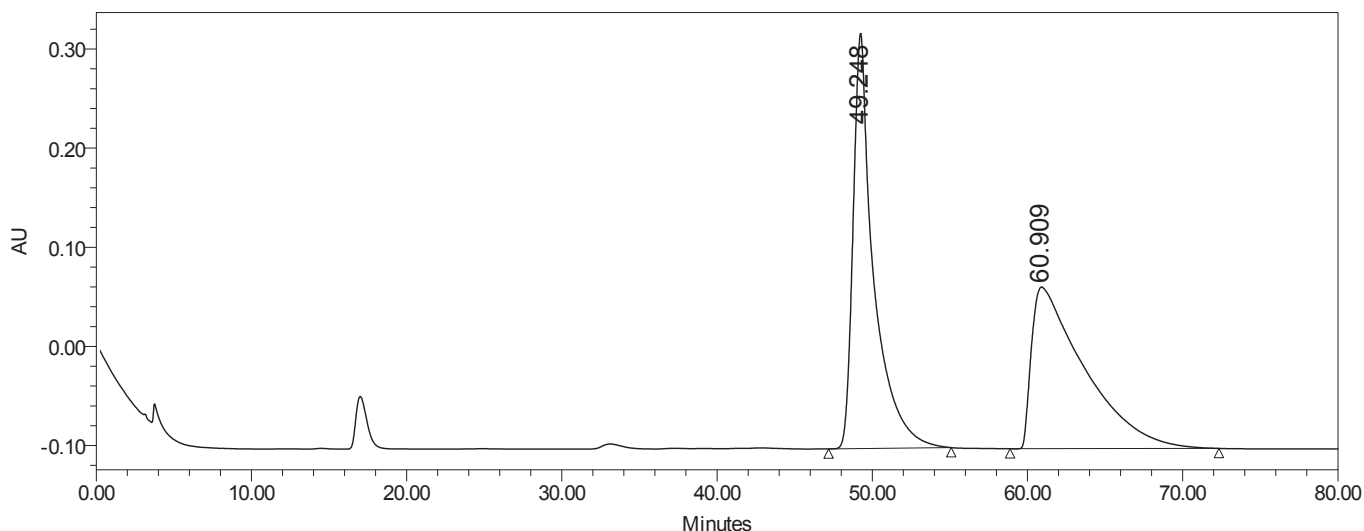




Injection Summary Report

SAMPLE INFORMATION

Sample Name:	avi_02_45_adh_99_1	Acquired By:	System
Sample Type:	Unknown	Sample Set Name	zdu09262013
Vial:	35	Acq. Method Set:	1_ADH 99_1 1mpm
Injection #:	1	Processing Method	02_45
Injection Volume:	10.00 ul	Channel Name:	W2489 ChB
Run Time:	80.0 Minutes	Proc. Chnl. Descr.:	W2489 ChB 220nm
Date Acquired:	9/27/2013 8:43:29 PM CDT		
Date Processed:	10/18/2013 5:42:45 PM CDT		



Channel: W2489 ChB; Processed Channel: W2489 ChB 220nm; Result Id: 8026; Processing Method: 02_45

Processed Channel Descr.: W2489 ChB 220nm

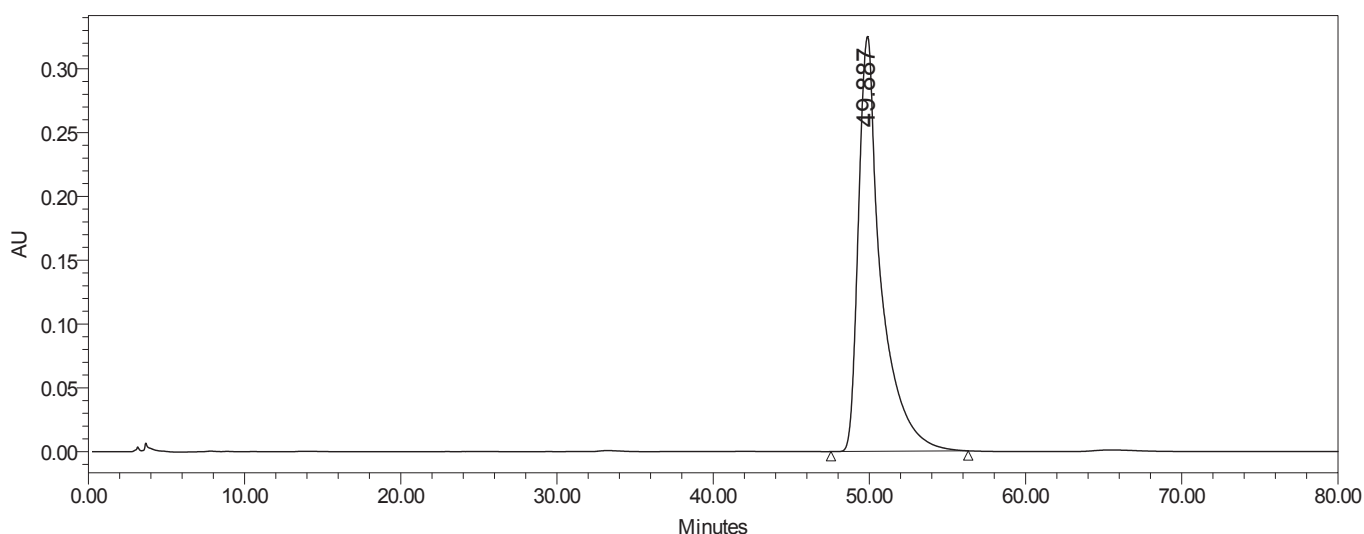
	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 220nm	49.248	38424855	49.87	418650
2	W2489 ChB 220nm	60.909	38617574	50.13	163028



Injection Summary Report

SAMPLE INFORMATION

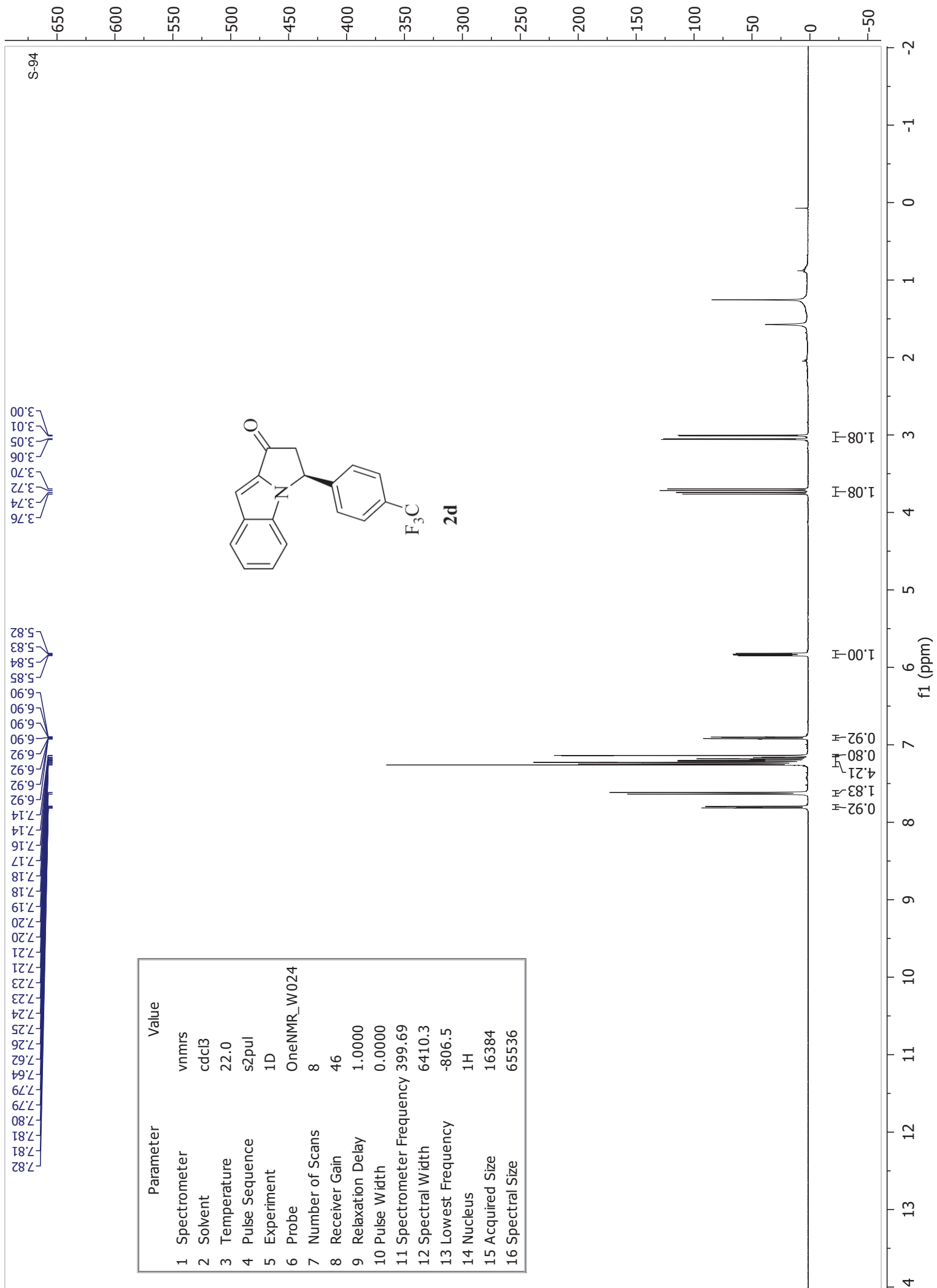
Sample Name:	avi_02_52_adh_99_1	Acquired By:	System
Sample Type:	Unknown	Sample Set Name	zdu09262013
Vial:	36	Acq. Method Set:	1_ADH 99_1 1mpm
Injection #:	1	Processing Method	02_52_99_1
Injection Volume:	10.00 ul	Channel Name:	W2489 ChB
Run Time:	80.0 Minutes	Proc. Chnl. Descr.:	W2489 ChB 220nm
Date Acquired:	9/27/2013 10:24:22 PM CDT		
Date Processed:	10/18/2013 5:44:55 PM CDT		

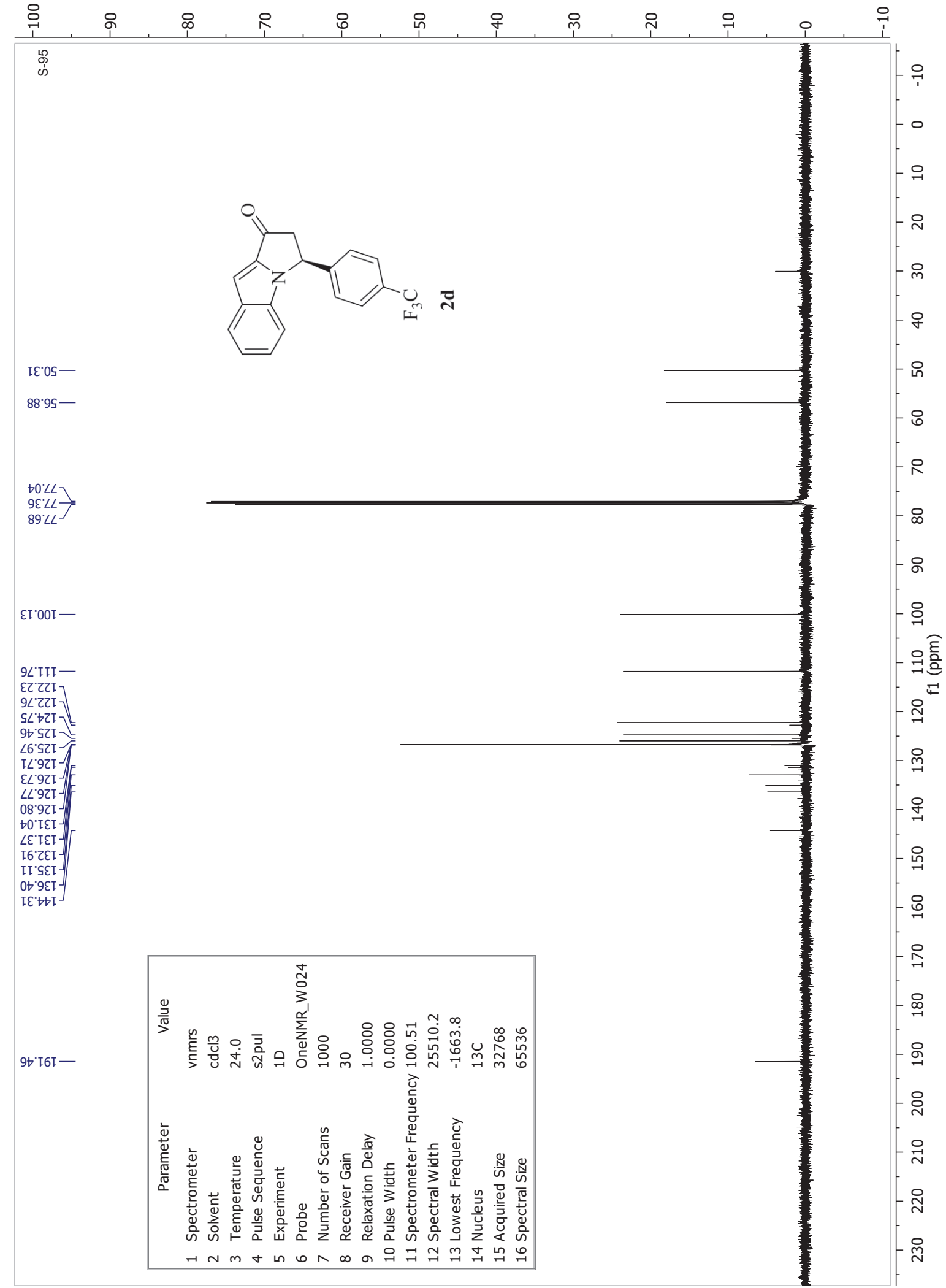


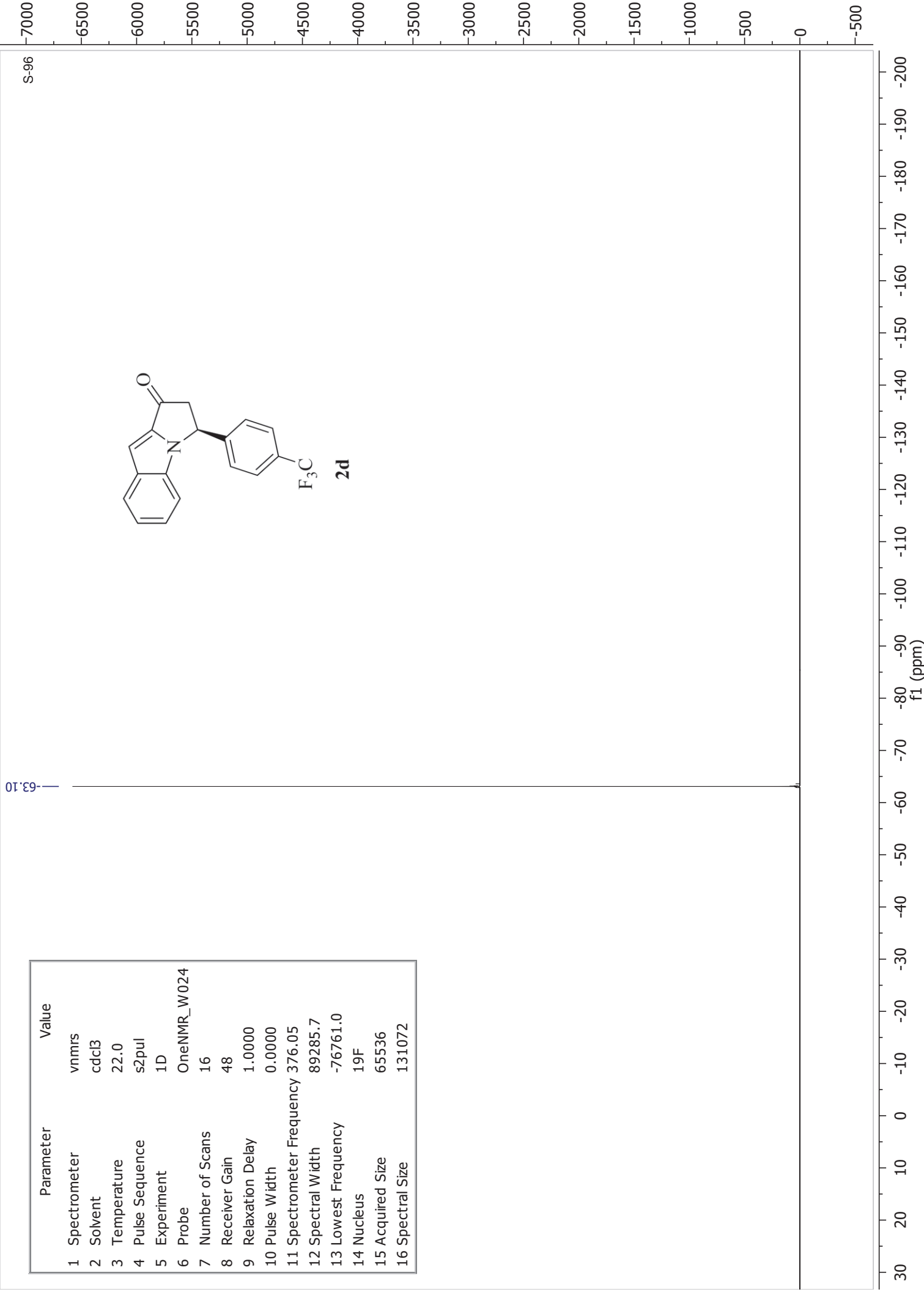
Channel: W2489 ChB; Processed Channel: W2489 ChB 220nm; Result Id: 8028; Processing Method: 02_52_99_1

Processed Channel Descr.: W2489 ChB 220nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 220nm	49.887	32482959	100.00	325129





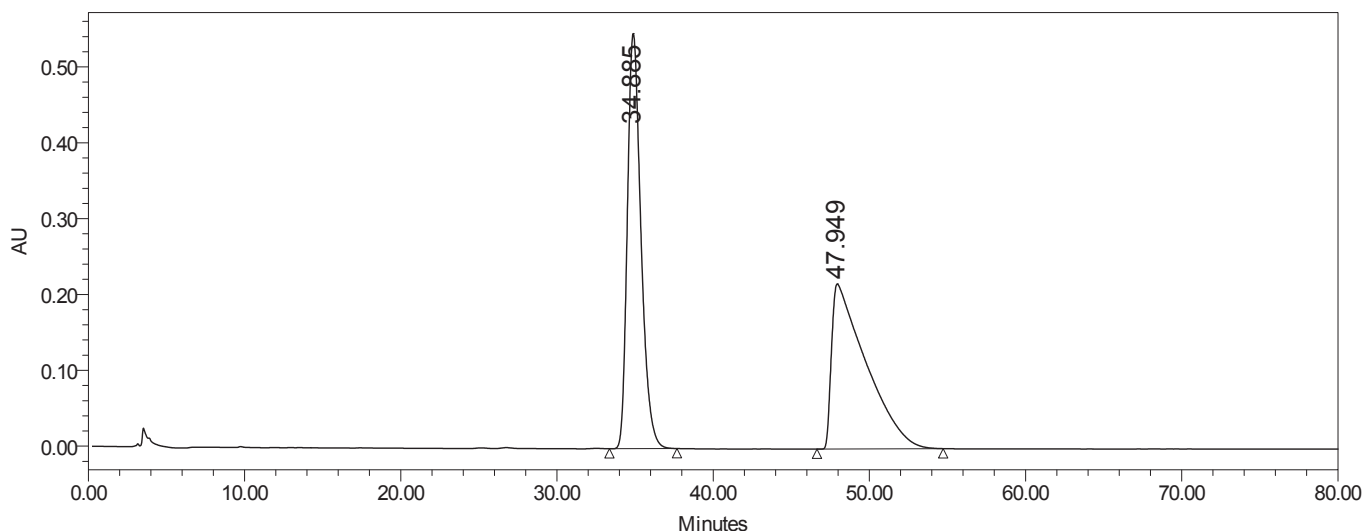




Injection Summary Report

SAMPLE INFORMATION

Sample Name:		Acquired By:	System
Sample Type:	Unknown	Sample Set Name	
Vial:	30	Acq. Method Set:	1_ADH 99_1 1mpm
Injection #:	1	Processing Method	69
Injection Volume:	10.00 ul	Channel Name:	W2489 ChB
Run Time:	80.0 Minutes	Proc. Chnl. Descr.:	W2489 ChB 220nm
Date Acquired:	2/13/2013 4:01:36 PM CST		
Date Processed:	9/24/2013 10:22:49 PM CDT		



Channel: W2489 ChB; Processed Channel: W2489 ChB 220nm; Result Id: 6821; Processing Method: 69

Processed Channel Descr.: W2489 ChB 220nm

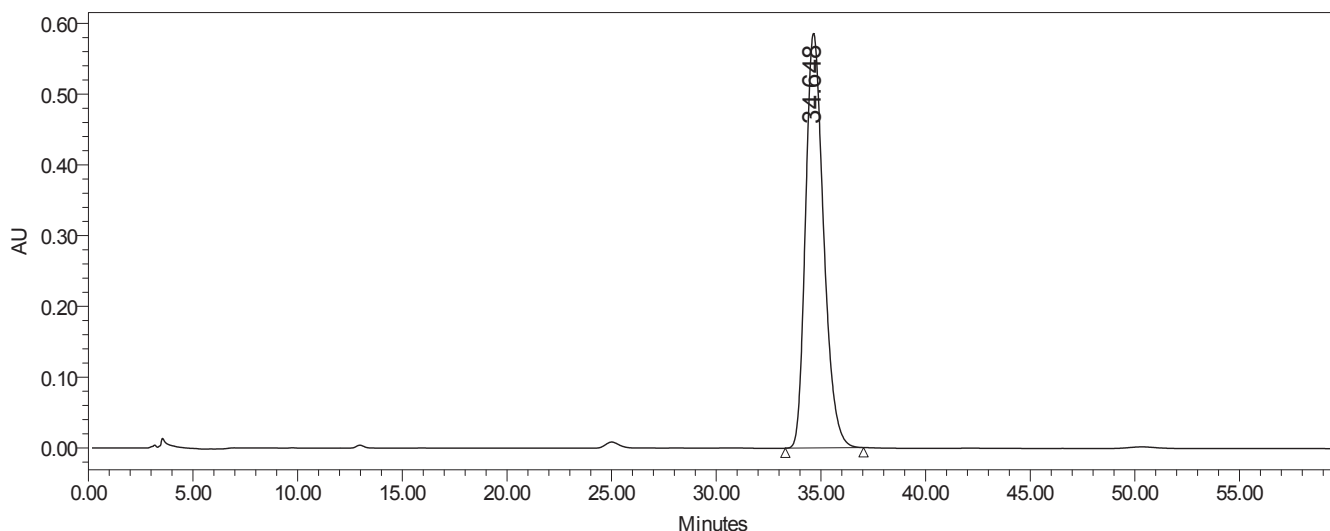
	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 220nm	34.885	33092264	49.86	547422
2	W2489 ChB 220nm	47.949	33284519	50.14	217544



Injection Summary Report

SAMPLE INFORMATION

Sample Name:		Acquired By:	System
Sample Type:	Unknown	Sample Set Name	
Vial:	60	Acq. Method Set:	1_ADH 99_1 1mpm
Injection #:	1	Processing Method	57
Injection Volume:	10.00 ul	Channel Name:	W2489 ChB
Run Time:	60.0 Minutes	Proc. Chnl. Descr.:	W2489 ChB 220nm
Date Acquired:	2/13/2013 1:21:37 PM CST		
Date Processed:	9/25/2013 5:19:45 PM CDT		

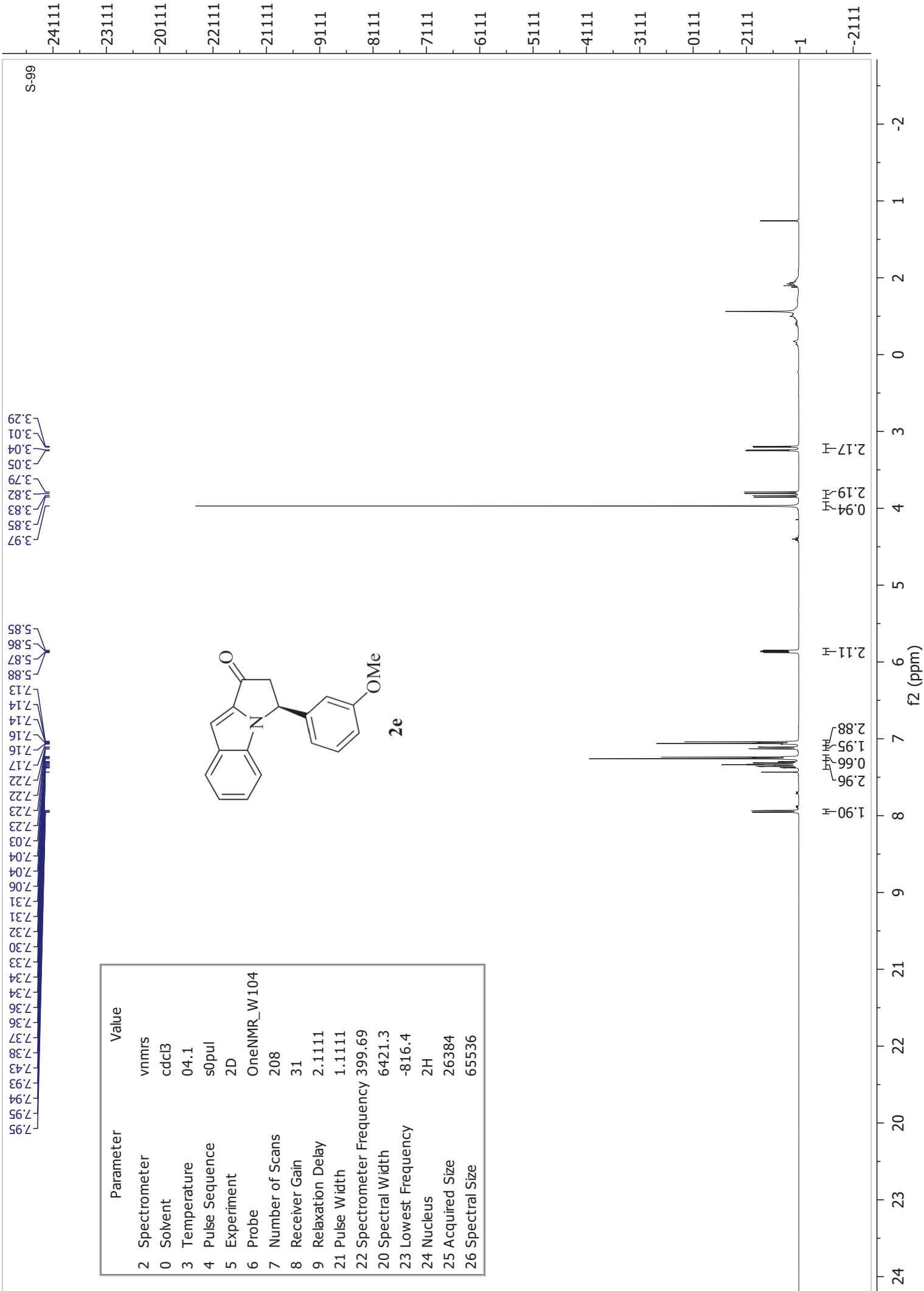


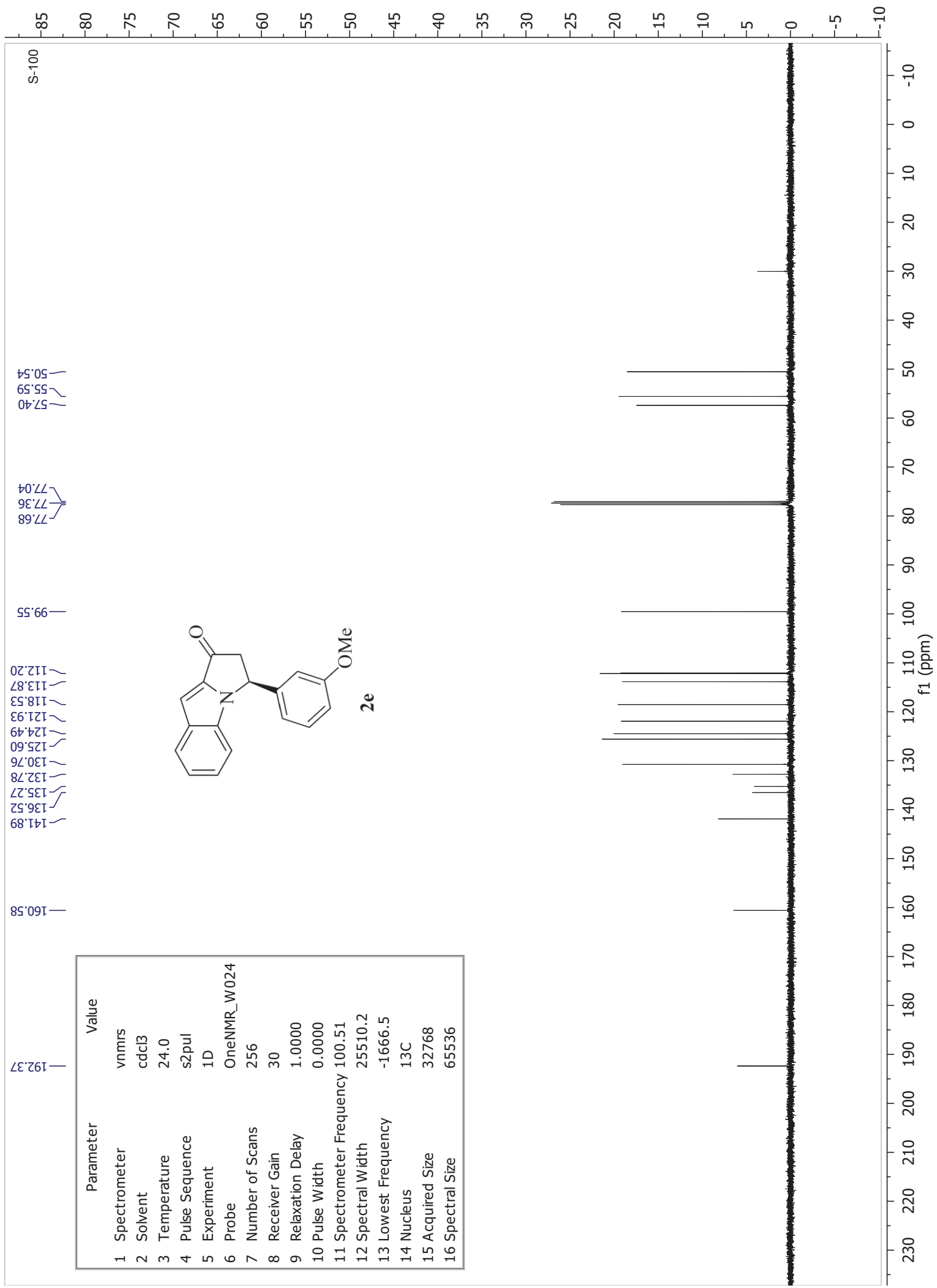
Channel: W2489 ChB; Processed Channel: W2489 ChB 220nm; Result Id: 6899; Processing Method: 57

Processed Channel Descr.: W2489 ChB 220nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 220nm	34.648	35099131	100.00	585834

Parameter	Value
2 Spectrometer	nmrs
0 Solvent	cdcl3
3 Temperature	04.1
4 Pulse Sequence	s0pul
5 Experiment	2D
6 Probe	OneNMR_W104
7 Number of Scans	208
8 Receiver Gain	31
9 Relaxation Delay	2.1111
21 Pulse Width	1.1111
22 Spectrometer Frequency	399.69
20 Spectral Width	6421.3
23 Lowest Frequency	-816.4
24 Nucleus	2H
25 Acquired Size	26384
26 Spectral Size	65536



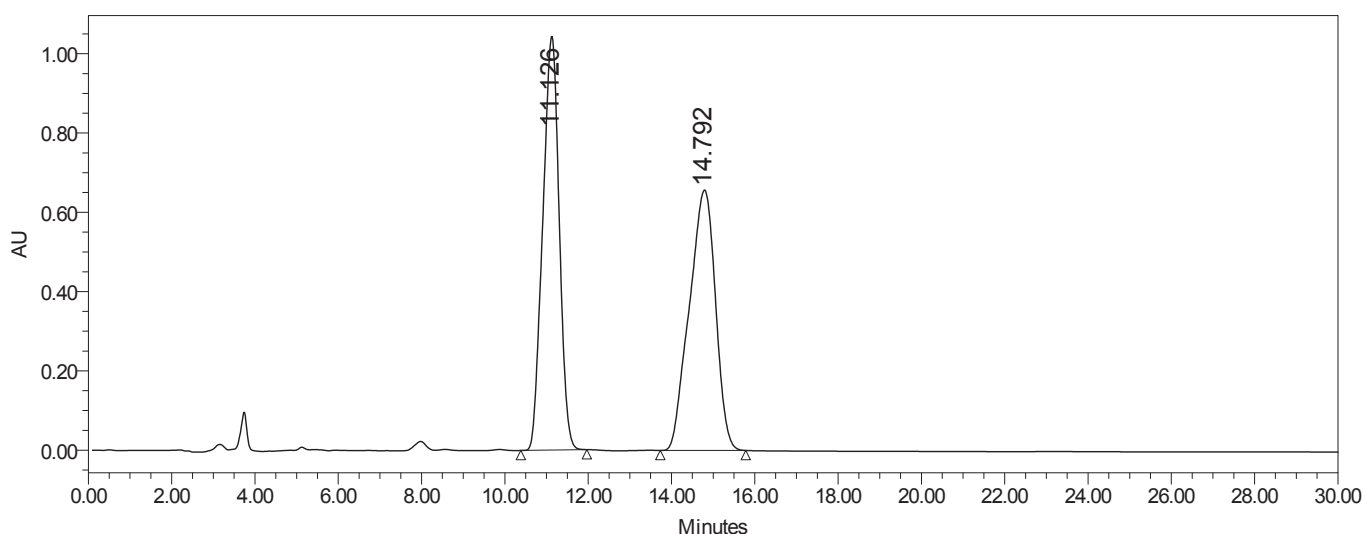




Injection Summary Report

SAMPLE INFORMATION

Sample Name:		Acquired By:	System
Sample Type:	Unknown	Sample Set Name	
Vial:	40	Acq. Method Set:	1_ADH 90_10 1mpm
Injection #:	1	Processing Method	01132
Injection Volume:	10.00 ul	Channel Name:	W2489 ChB
Run Time:	30.0 Minutes	Proc. Chnl. Descr.:	W2489 ChB 220nm
Date Acquired:	9/6/2012 8:42:49 AM CDT		
Date Processed:	9/24/2013 10:00:24 PM CDT		



Channel: W2489 ChB; Processed Channel: W2489 ChB 220nm; Result Id: 6805; Processing Method: 01132

Processed Channel Descr.: W2489 ChB 220nm

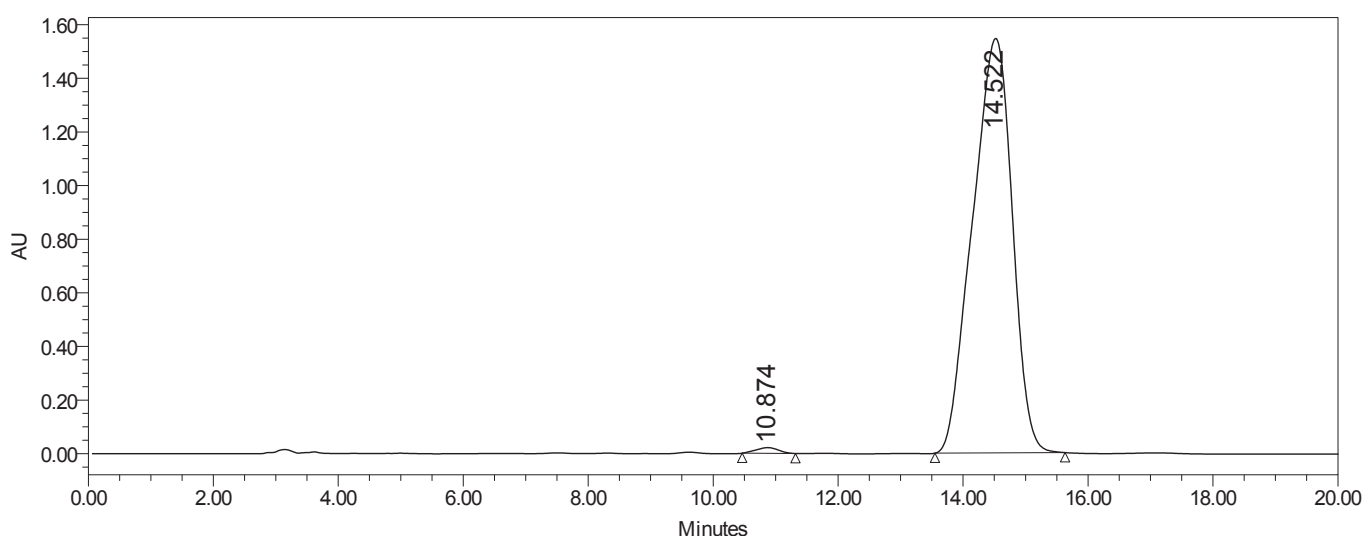
	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 220nm	11.126	28573731	49.90	1044313
2	W2489 ChB 220nm	14.792	28687952	50.10	656908



Injection Summary Report

SAMPLE INFORMATION

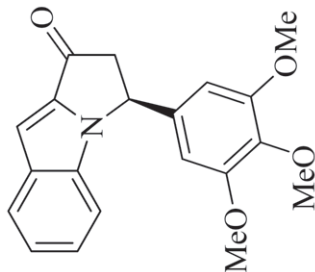
Sample Name:		Acquired By:	System
Sample Type:	Unknown	Sample Set Name	
Vial:	41	Acq. Method Set:	1_ADH 90_10 1mpm
Injection #:	1	Processing Method	131
Injection Volume:	10.00 ul	Channel Name:	W2489 ChB
Run Time:	20.0 Minutes	Proc. Chnl. Descr.:	W2489 ChB 220nm
Date Acquired:	9/6/2012 2:54:34 PM CDT		
Date Processed:	9/24/2013 10:02:13 PM CDT		

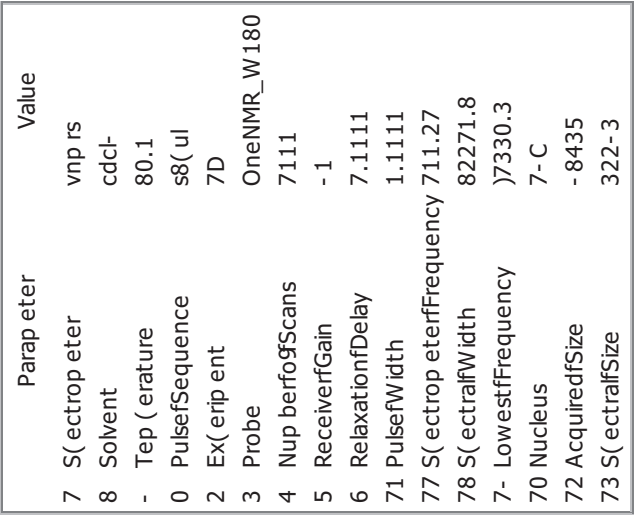


Channel: W2489 ChB; Processed Channel: W2489 ChB 220nm; Result Id: 6807; Processing Method: 131

Processed Channel Descr.: W2489 ChB 220nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 220nm	10.874	530321	0.77	21264
2	W2489 ChB 220nm	14.522	68186947	99.23	1545966



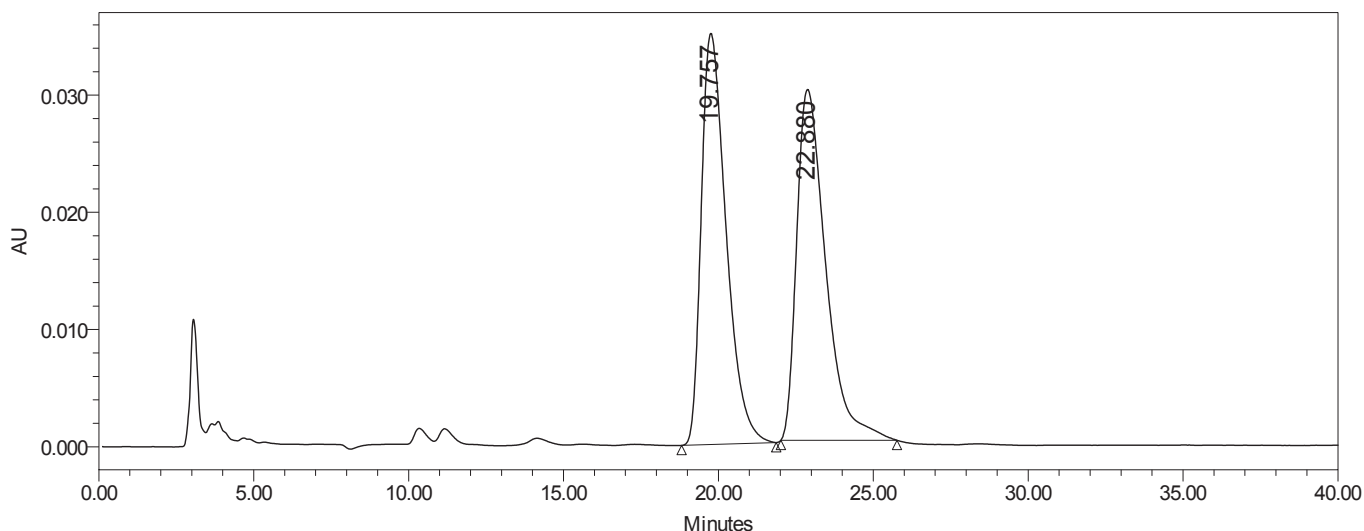




Injection Summary Report

SAMPLE INFORMATION

Sample Name:	avi_105_2_adh_90_10	Acquired By:	System
Sample Type:	Unknown	Sample Set Name	avi_nov_5_2013
Vial:	111	Acq. Method Set:	1_ADH 90_10 1mpm
Injection #:	1	Processing Method	105_2
Injection Volume:	10.00 ul	Channel Name:	W2489 ChB
Run Time:	40.0 Minutes	Proc. Chnl. Descr.:	W2489 ChB 220nm
Date Acquired:	11/5/2013 11:19:44 PM CST		
Date Processed:	11/6/2013 9:56:51 AM CST		



Channel: W2489 ChB; Processed Channel: W2489 ChB 220nm; Result Id: 8265; Processing Method: 105_2

Processed Channel Descr.: W2489 ChB 220nm

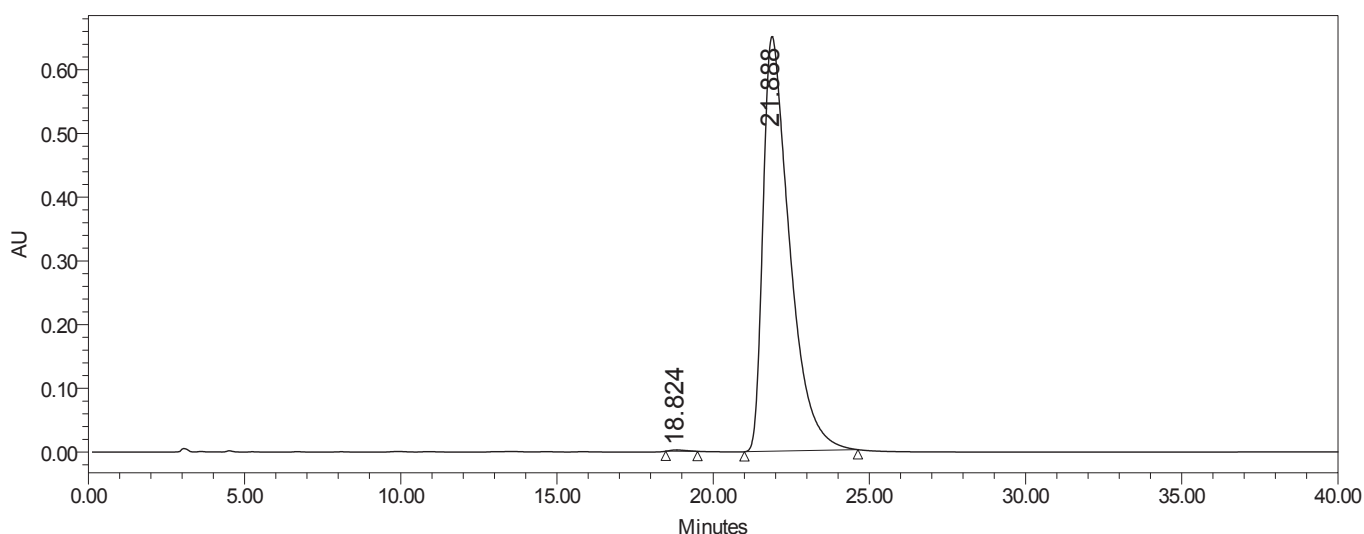
	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 220nm	19.757	1952173	50.02	35081
2	W2489 ChB 220nm	22.880	1950334	49.98	29938



Injection Summary Report

SAMPLE INFORMATION

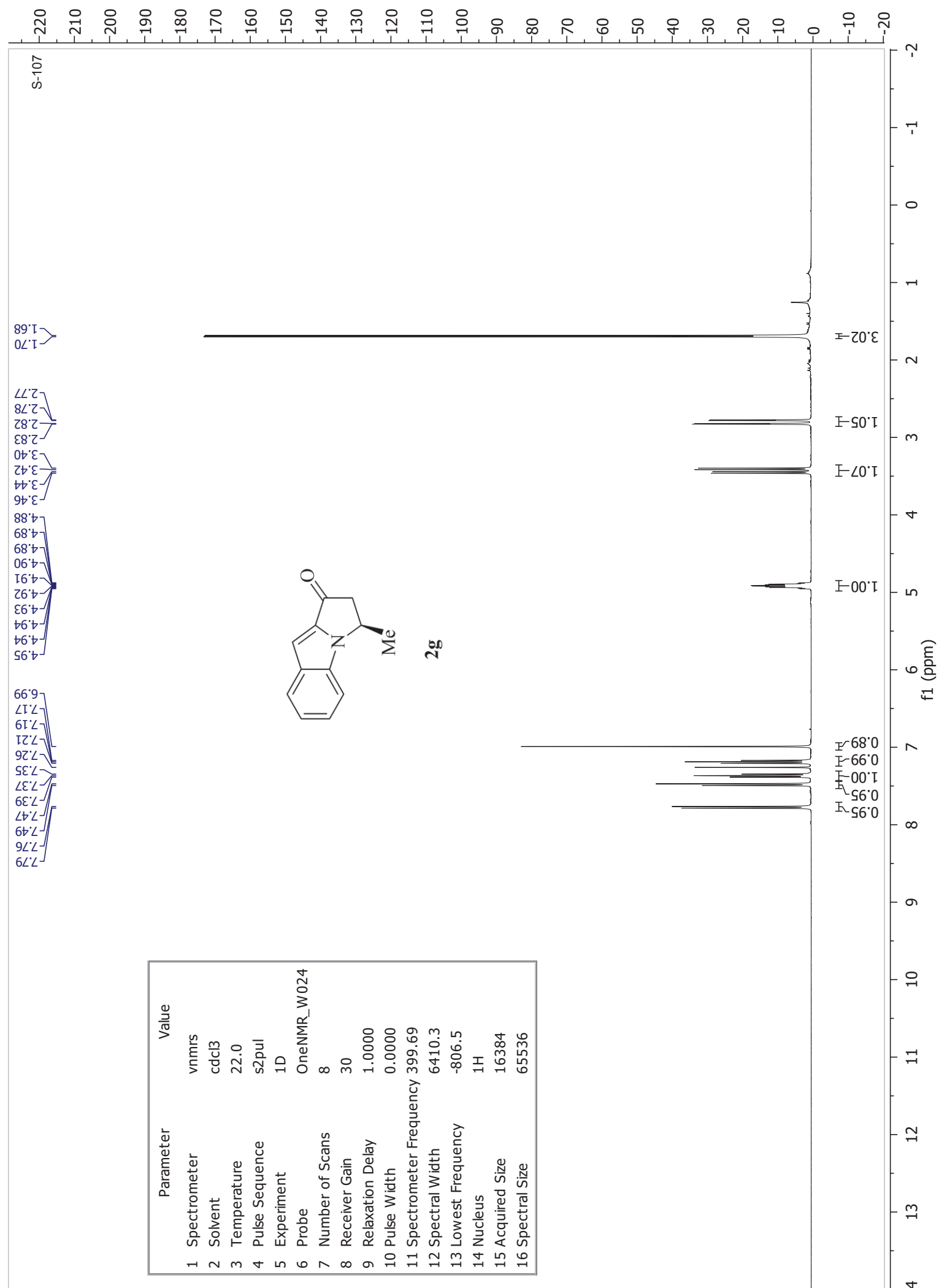
Sample Name:	avi_nb_02_104_adh_90_10	Acquired By:	System
Sample Type:	Unknown	Sample Set Name	adu04012013
Vial:	44	Acq. Method Set:	1_ADH 90_10 1mpm
Injection #:	1	Processing Method	104
Injection Volume:	10.00 ul	Channel Name:	W2489 ChB
Run Time:	40.0 Minutes	Proc. Chnl. Descr.:	W2489 ChB 220nm
Date Acquired:	4/1/2013 4:04:28 PM CDT		
Date Processed:	9/9/2013 6:39:31 PM CDT		

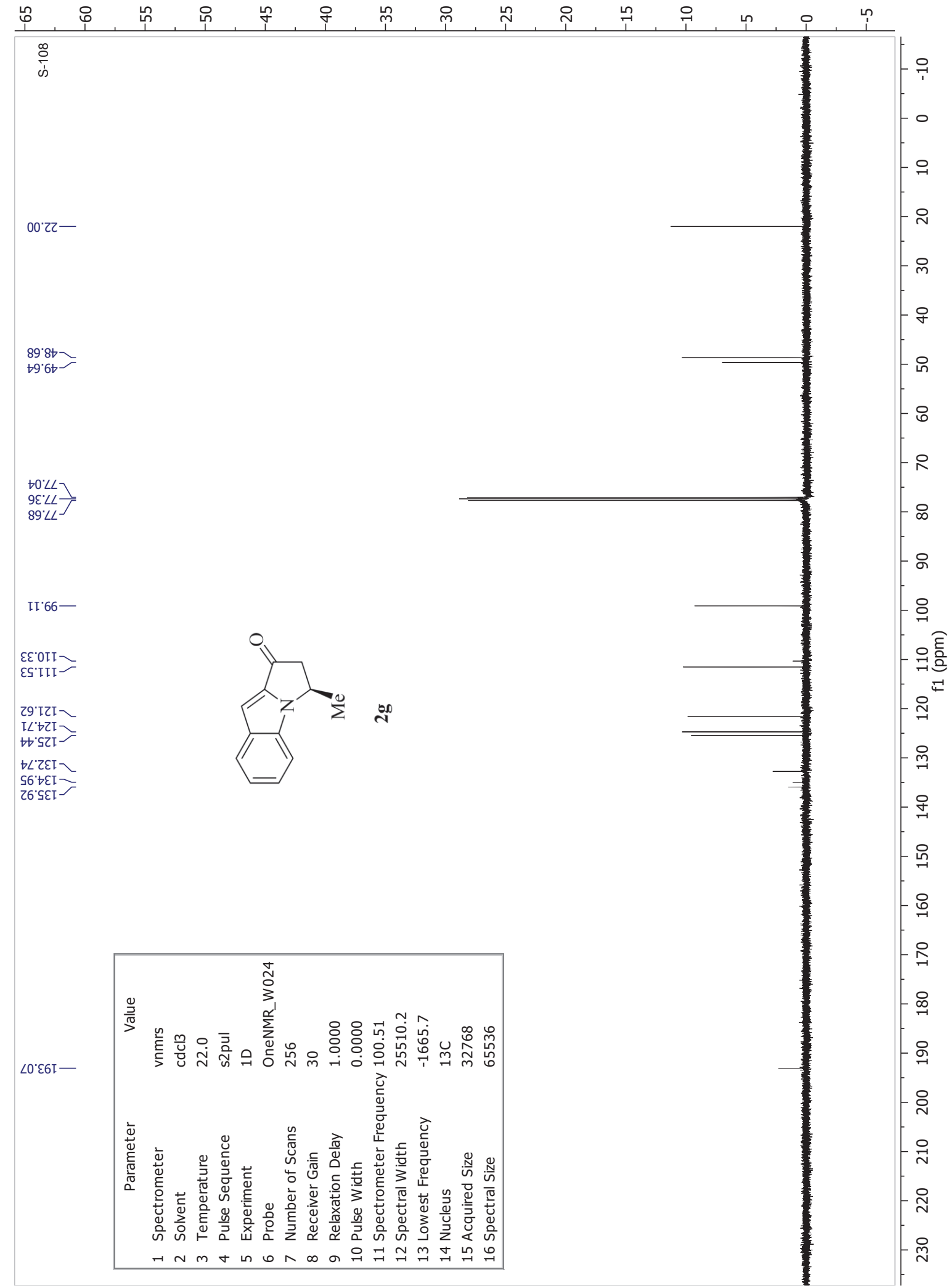


Channel: W2489 ChB; Processed Channel: W2489 ChB 220nm; Result Id: 6265; Processing Method: 104

Processed Channel Descr.: W2489 ChB 220nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 220nm	18.824	69390	0.18	2029
2	W2489 ChB 220nm	21.888	38421158	99.82	651068



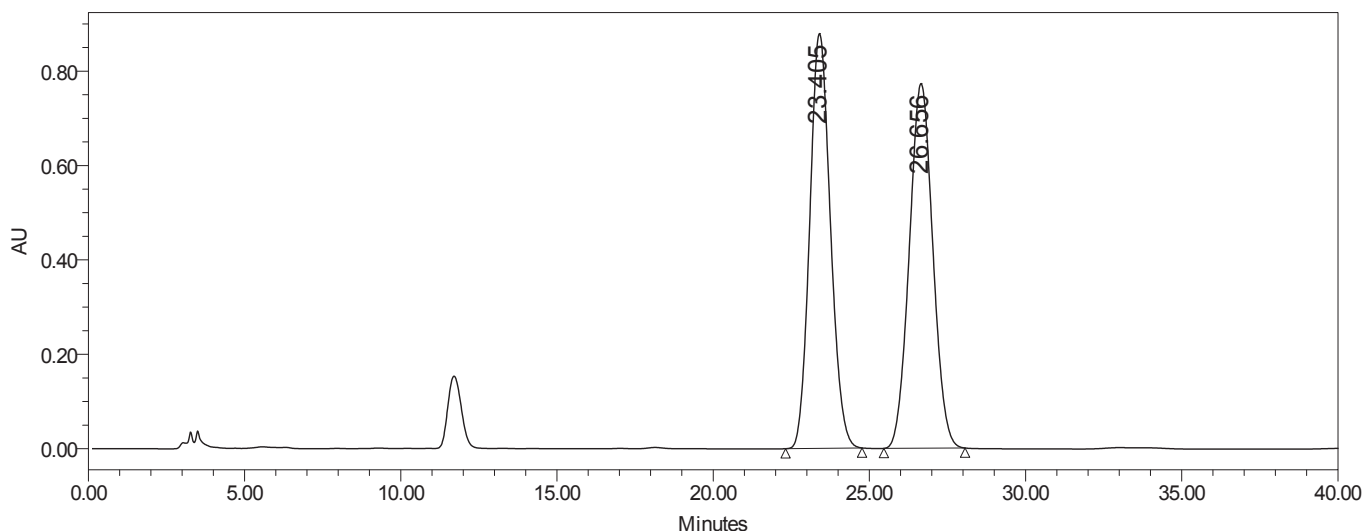




Injection Summary Report

SAMPLE INFORMATION

Sample Name:	avi_159_adh99-1_1mpm	Acquired By:	System
Sample Type:	Unknown	Sample Set Name	
Vial:	63	Acq. Method Set:	1_ADH 99_1 1mpm
Injection #:	1	Processing Method	159
Injection Volume:	10.00 ul	Channel Name:	W2489 ChB
Run Time:	40.0 Minutes	Proc. Chnl. Descr.:	W2489 ChB 220nm
Date Acquired:	10/31/2012 12:41:44 PM CDT		
Date Processed:	9/24/2013 10:08:18 PM CDT		



Channel: W2489 ChB; Processed Channel: W2489 ChB 220nm; Result Id: 6809; Processing Method: 159

Processed Channel Descr.: W2489 ChB 220nm

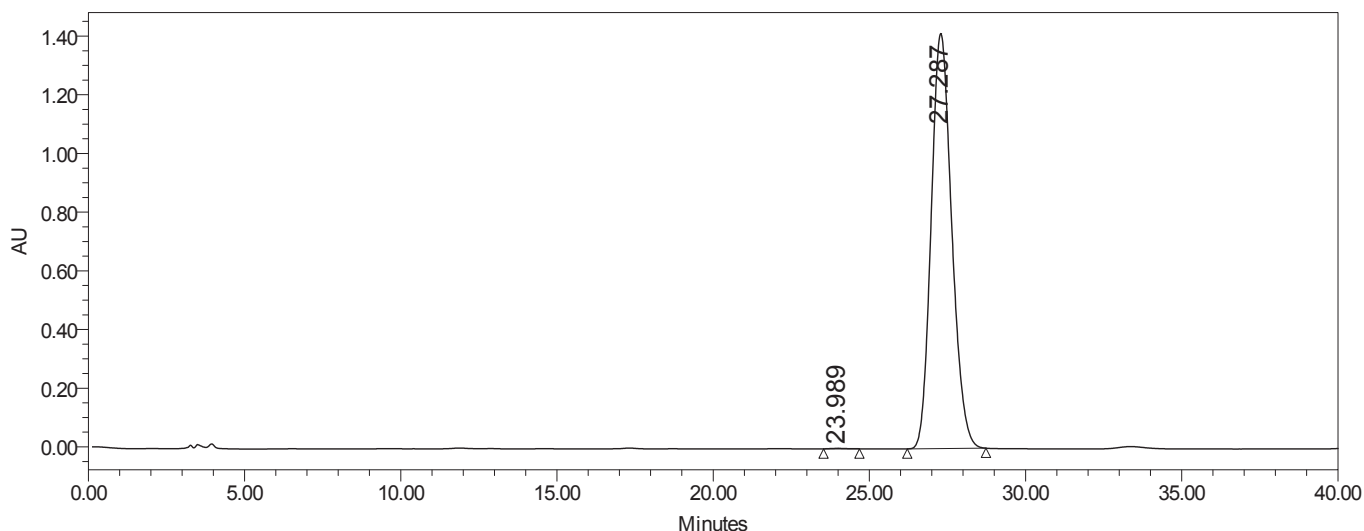
	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 220nm	23.405	40327812	50.01	879004
2	W2489 ChB 220nm	26.656	40304215	49.99	772539



Injection Summary Report

SAMPLE INFORMATION

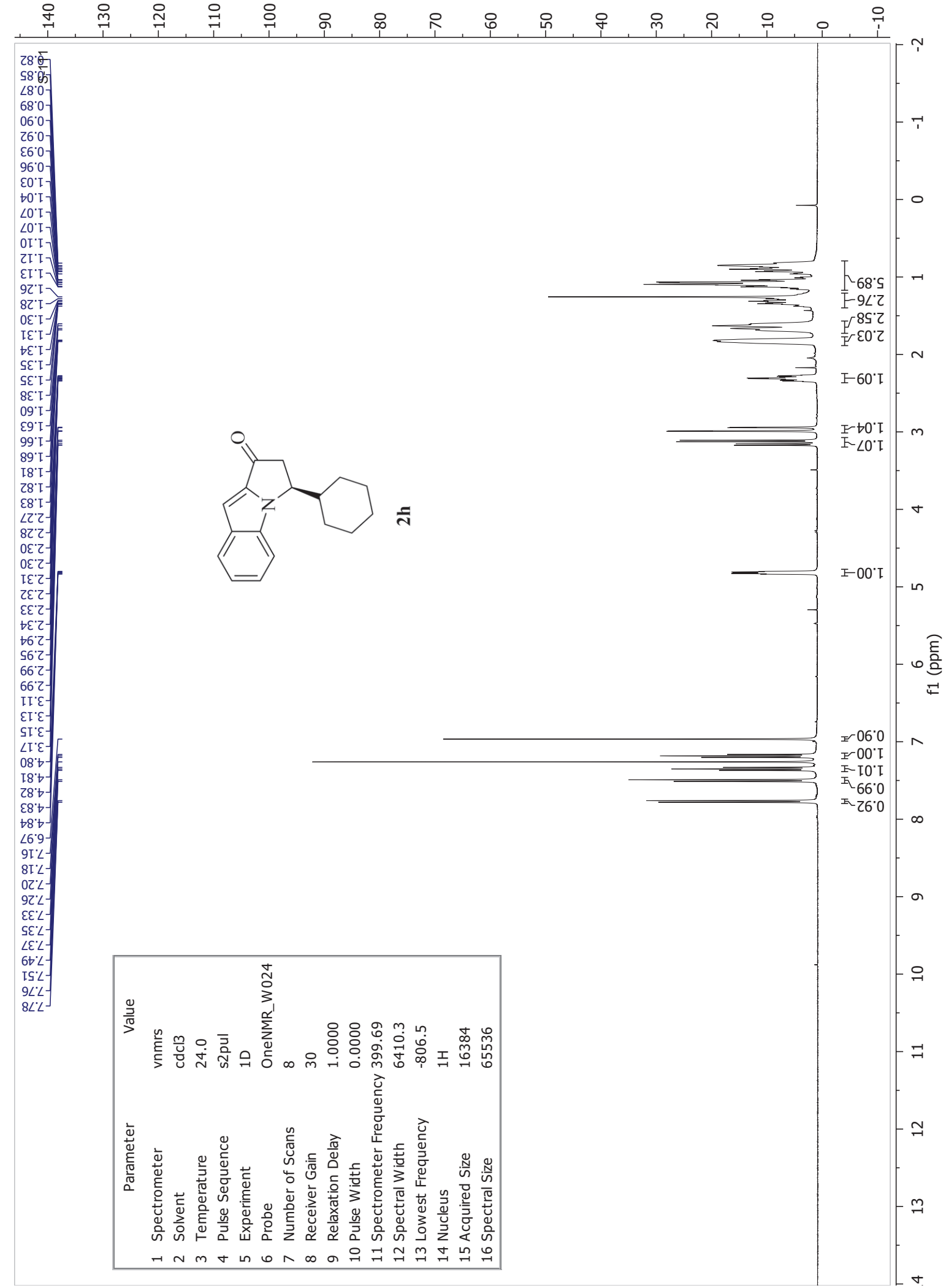
Sample Name:	avi_158_adh99-1_1mpm_3	Acquired By:	System
Sample Type:	Unknown	Sample Set Name	
Vial:	90	Acq. Method Set:	1_ADH 99_1 1mpm
Injection #:	1	Processing Method	158
Injection Volume:	10.00 ul	Channel Name:	W2489 ChB
Run Time:	40.0 Minutes	Proc. Chnl. Descr.:	W2489 ChB 220nm
Date Acquired:	10/31/2012 4:11:10 PM CDT		
Date Processed:	9/24/2013 10:10:03 PM CDT		



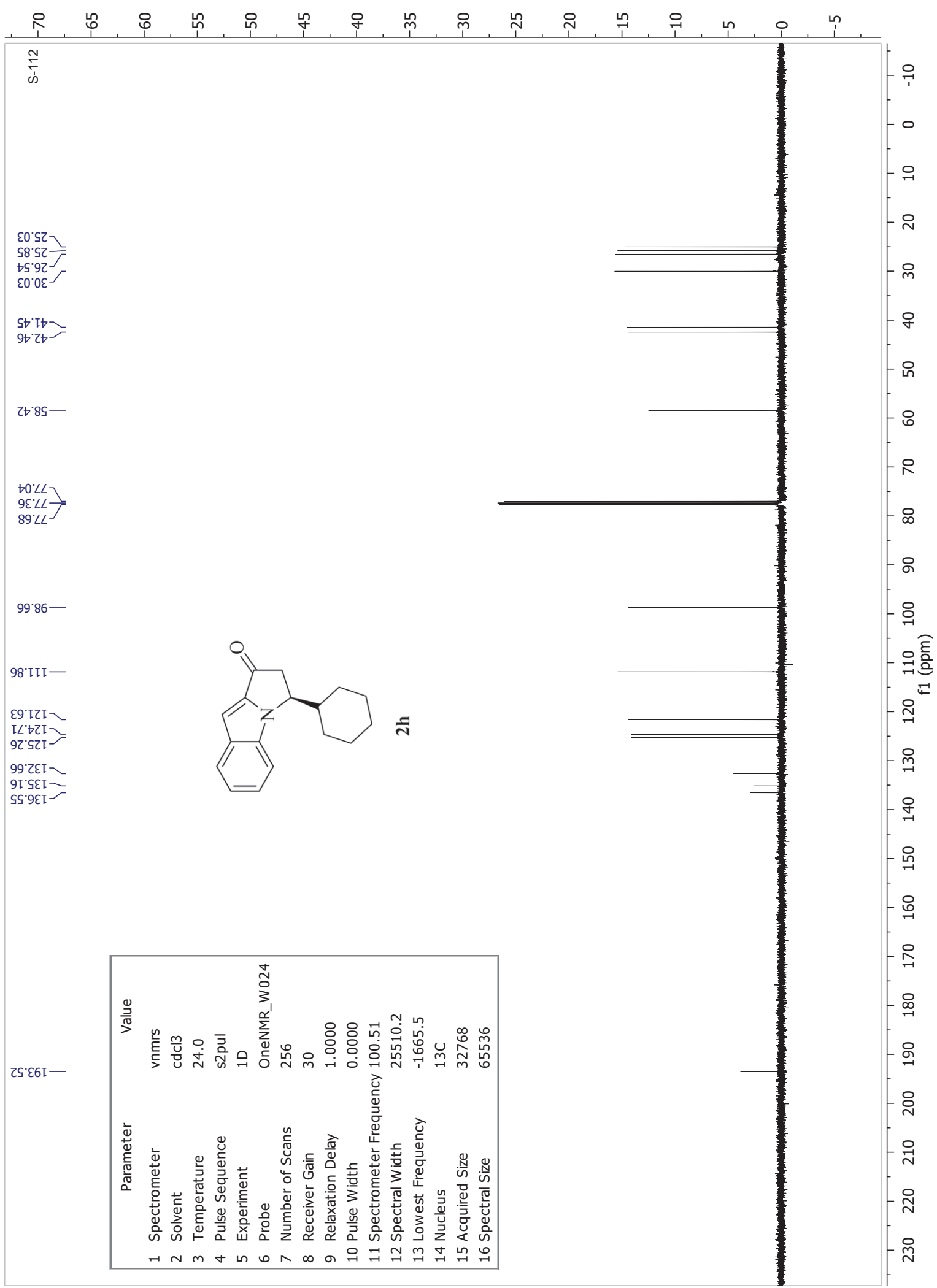
Channel: W2489 ChB; Processed Channel: W2489 ChB 220nm; Result Id: 6811; Processing Method: 158

Processed Channel Descr.: W2489 ChB 220nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 220nm	23.989	52755	0.08	1531
2	W2489 ChB 220nm	27.287	64681529	99.92	1414997



Parameter	Value
1 Spectrometer	nmrs
2 Solvent	cdcl3
3 Temperature	24.0
4 Pulse Sequence	s2pul
5 Experiment	1D
6 Probe	OneNMR_W024
7 Number of Scans	8
8 Receiver Gain	30
9 Relaxation Delay	1.0000
10 Pulse Width	0.0000
11 Spectrometer Frequency	399.69
12 Spectral Width	6410.3
13 Lowest Frequency	-806.5
14 Nucleus	1H
15 Acquired Size	16384
16 Spectral Size	65536

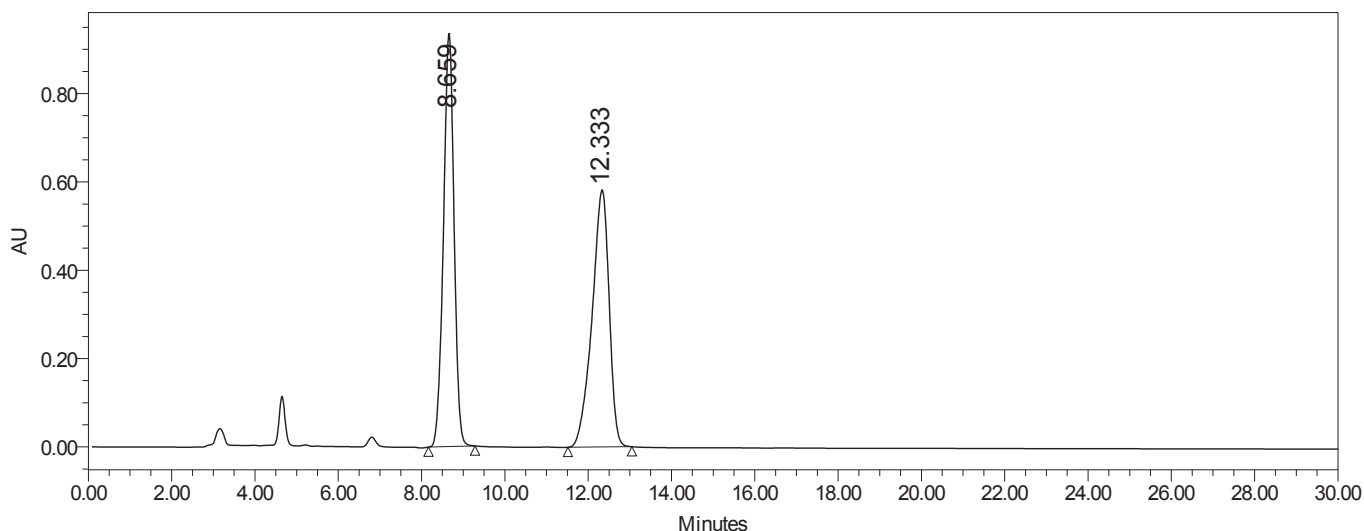




Injection Summary Report

SAMPLE INFORMATION

Sample Name:		Acquired By:	System
Sample Type:	Unknown	Sample Set Name	
Vial:	2	Acq. Method Set:	1_ADH 95_5 1mpm
Injection #:	1	Processing Method	123
Injection Volume:	10.00 ul	Channel Name:	W2489 ChB
Run Time:	30.0 Minutes	Proc. Chnl. Descr.:	W2489 ChB 220nm
Date Acquired:	8/21/2012 8:42:29 PM CDT		
Date Processed:	9/22/2013 8:15:45 PM CDT		



Channel: W2489 ChB; Processed Channel: W2489 ChB 220nm; Result Id: 6687; Processing Method: 123

Processed Channel Descr.: W2489 ChB 220nm

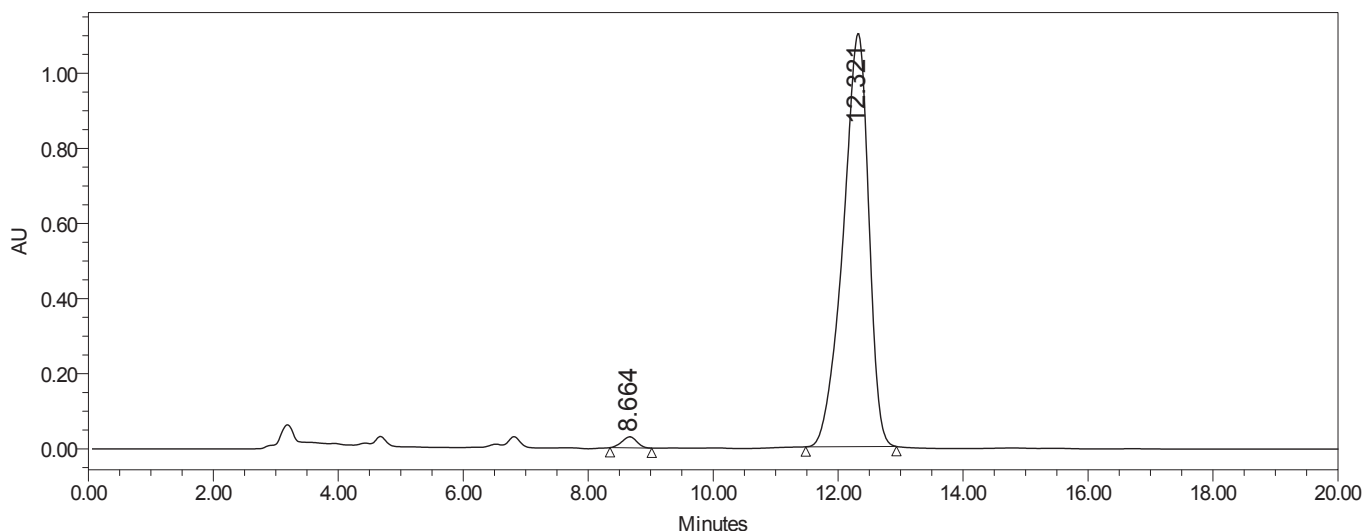
	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 220nm	8.659	16478822	49.91	937497
2	W2489 ChB 220nm	12.333	16536508	50.09	581580



Injection Summary Report

SAMPLE INFORMATION

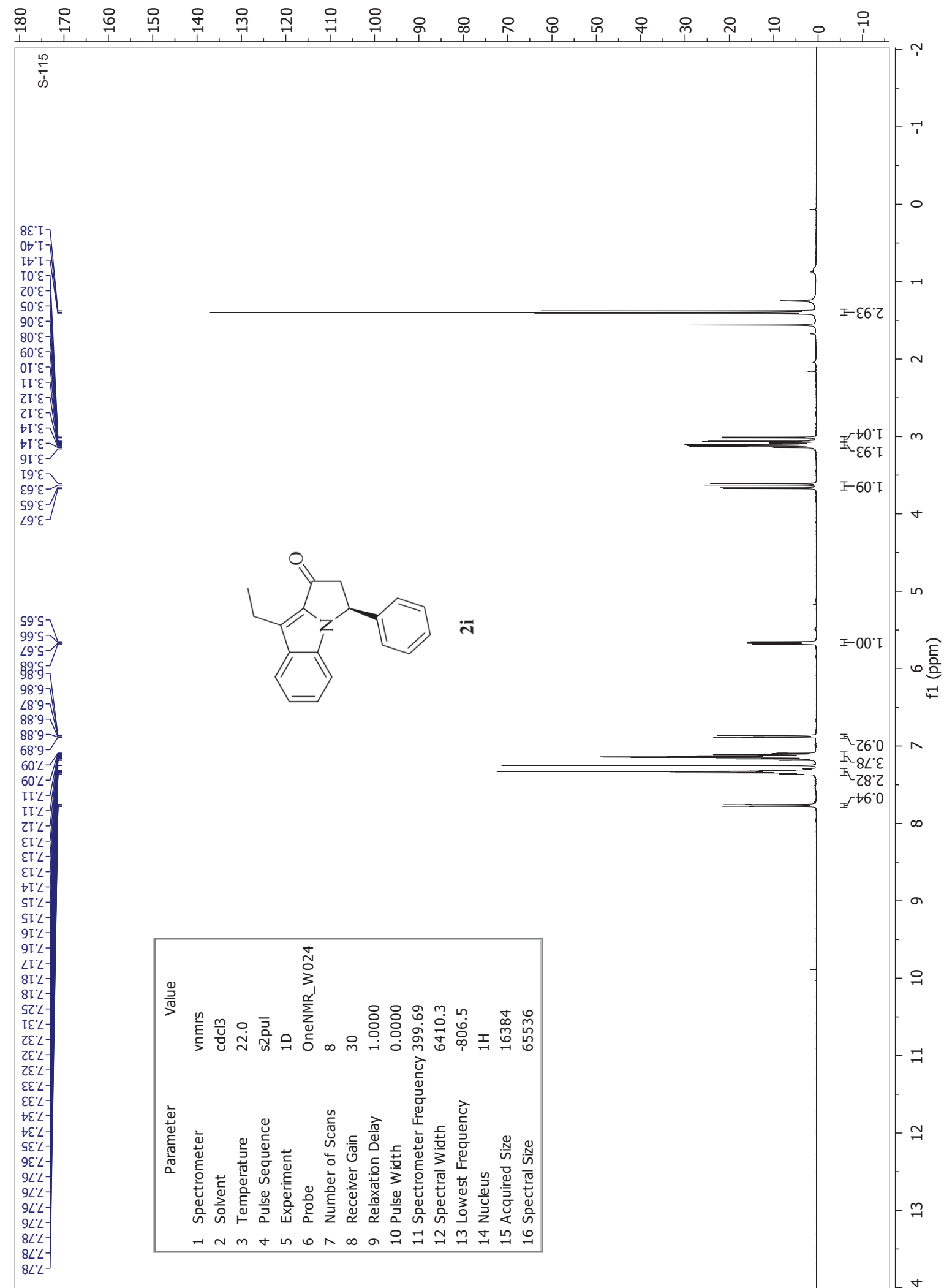
Sample Name:		Acquired By:	System
Sample Type:	Unknown	Sample Set Name	
Vial:	26	Acq. Method Set:	1_ADH 95_5 1mpm
Injection #:	1	Processing Method	124
Injection Volume:	10.00 ul	Channel Name:	W2489 ChB
Run Time:	20.0 Minutes	Proc. Chnl. Descr.:	W2489 ChB 220nm
Date Acquired:	8/21/2012 10:44:41 PM CDT		
Date Processed:	9/22/2013 8:18:05 PM CDT		

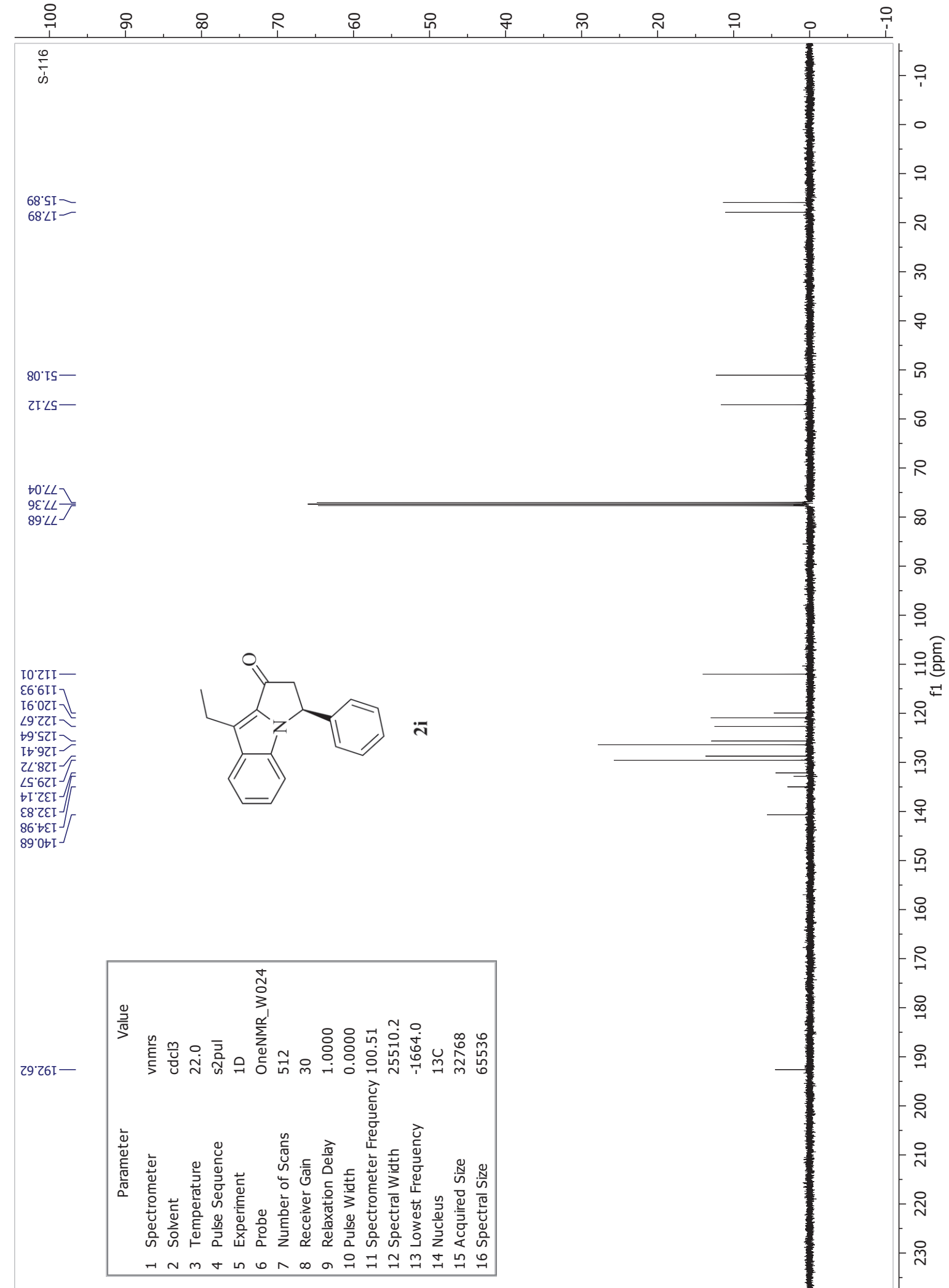


Channel: W2489 ChB; Processed Channel: W2489 ChB 220nm; Result Id: 6689; Processing Method: 124

Processed Channel Descr.: W2489 ChB 220nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 220nm	8.664	487904	1.54	29352
2	W2489 ChB 220nm	12.321	31194120	98.46	1100146



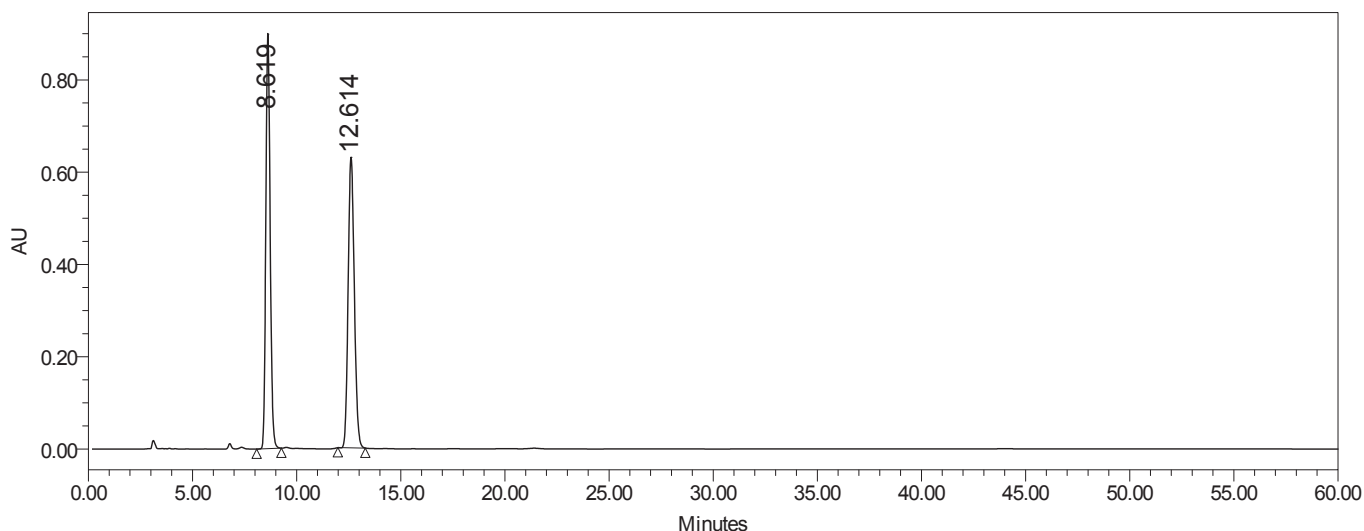




Injection Summary Report

SAMPLE INFORMATION

Sample Name:	avi_nb_02_147_odh_95_5	Acquired By:	System
Sample Type:	Unknown	Sample Set Name	avi_june10_2013
Vial:	90	Acq. Method Set:	3_ODH 95_5 1mpm
Injection #:	1	Processing Method	147
Injection Volume:	10.00 ul	Channel Name:	W2489 ChB
Run Time:	60.0 Minutes	Proc. Chnl. Descr.:	W2489 ChB 220nm
Date Acquired:	6/11/2013 3:18:32 PM CDT		
Date Processed:	9/9/2013 5:51:17 PM CDT		



Channel: W2489 ChB; Processed Channel: W2489 ChB 220nm; Result Id: 6253; Processing Method: 147

Processed Channel Descr.: W2489 ChB 220nm

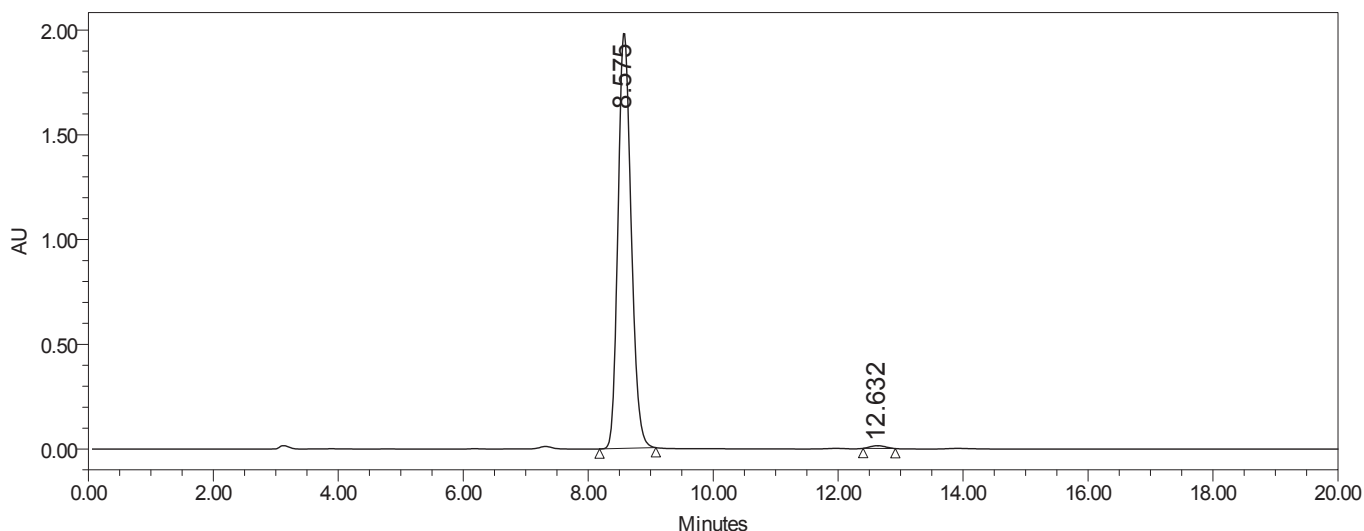
	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 220nm	8.619	13022025	50.07	899895
2	W2489 ChB 220nm	12.614	12987815	49.93	630046



Injection Summary Report

SAMPLE INFORMATION

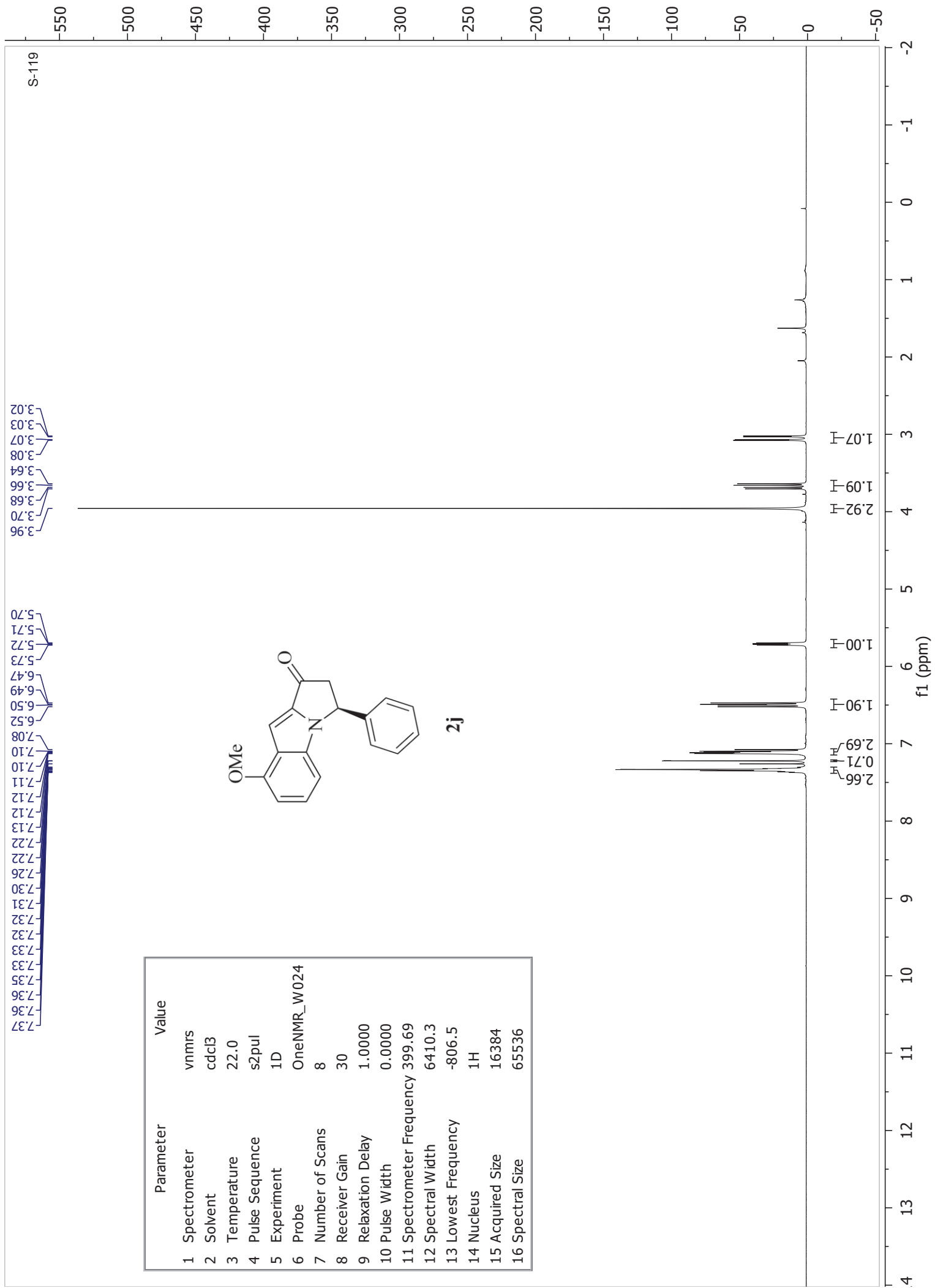
Sample Name:	avi_nb_02_146_odh_95_5	Acquired By:	System
Sample Type:	Unknown	Sample Set Name	avi_june10_2013
Vial:	91	Acq. Method Set:	3_ODH 95_5 1mpm
Injection #:	1	Processing Method	146
Injection Volume:	10.00 ul	Channel Name:	W2489 ChB
Run Time:	20.0 Minutes	Proc. Chnl. Descr.:	W2489 ChB 220nm
Date Acquired:	6/11/2013 4:55:17 PM CDT		
Date Processed:	9/9/2013 5:53:55 PM CDT		

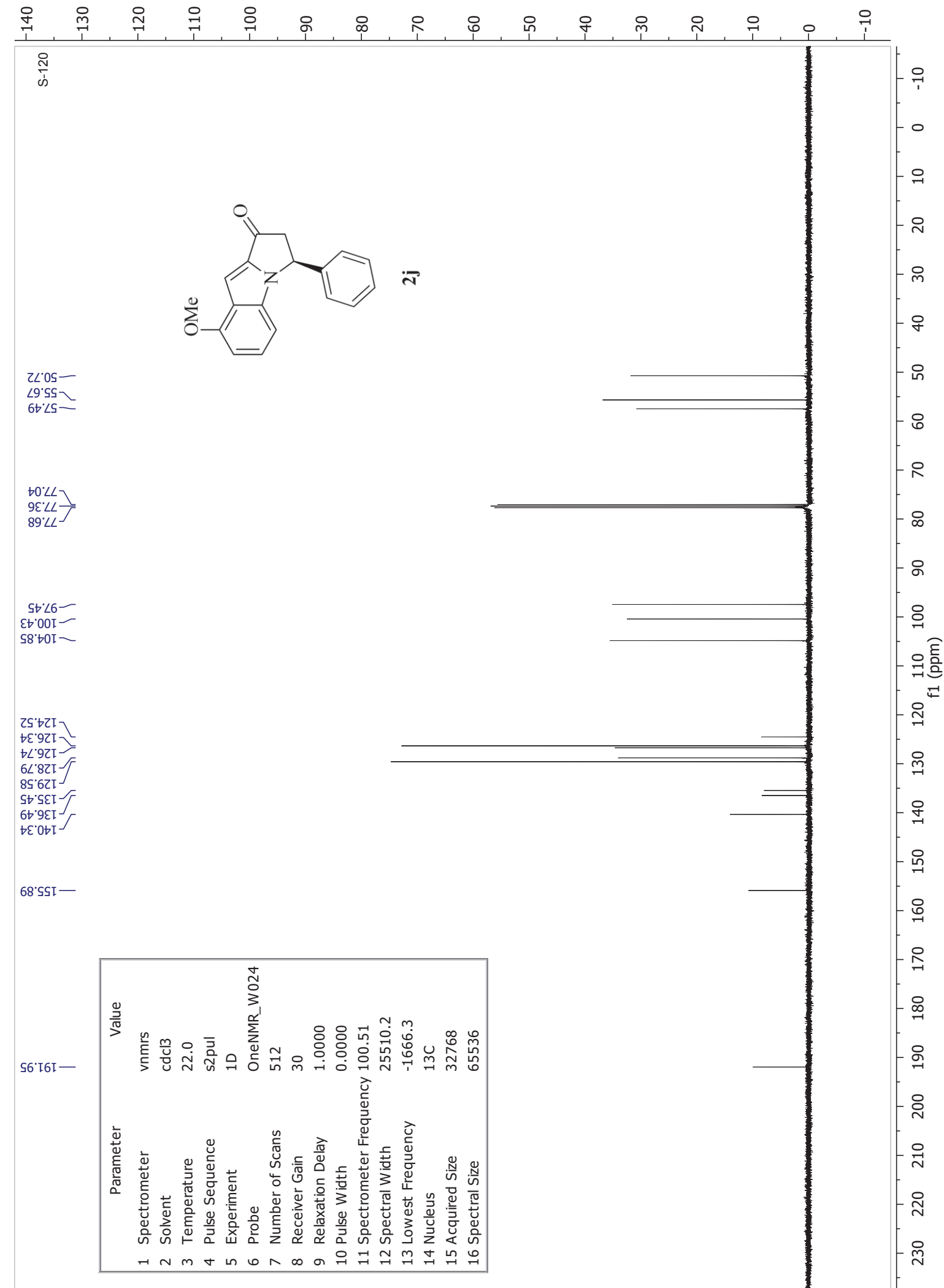


Channel: W2489 ChB; Processed Channel: W2489 ChB 220nm; Result Id: 6255; Processing Method: 146

Processed Channel Descr.: W2489 ChB 220nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 220nm	8.575	29036295	99.24	1986547
2	W2489 ChB 220nm	12.632	222051	0.76	13317



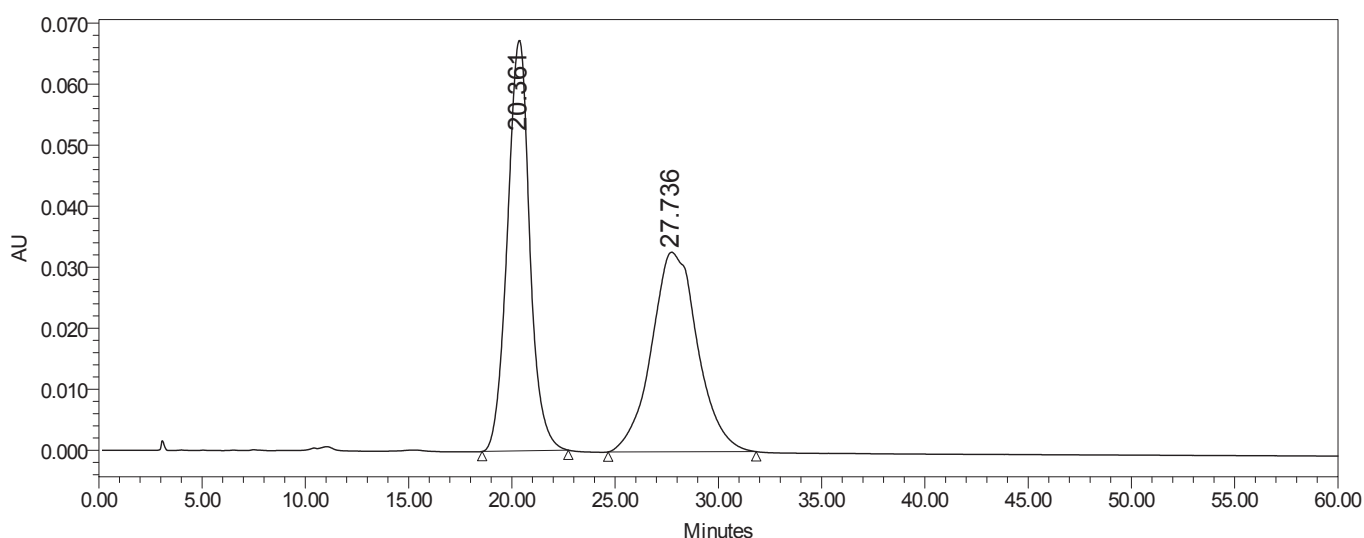




Injection Summary Report

SAMPLE INFORMATION

Sample Name:	avi_109_adh_95_5_50	Acquired By:	System
Sample Type:	Unknown	Sample Set Name	avi_sep2_2013
Vial:	20	Acq. Method Set:	1_ADH 95_5 1mpm
Injection #:	1	Processing Method	avi_109
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	60.0 Minutes	Proc. Chnl. Descr.:	W2489 ChA 254nm
Date Acquired: 9/3/2013 1:23:10 PM CDT			
Date Processed: 9/3/2013 8:01:31 PM CDT			



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 6038; Processing Method: avi_109

Processed Channel Descr.: W2489 ChA 254nm

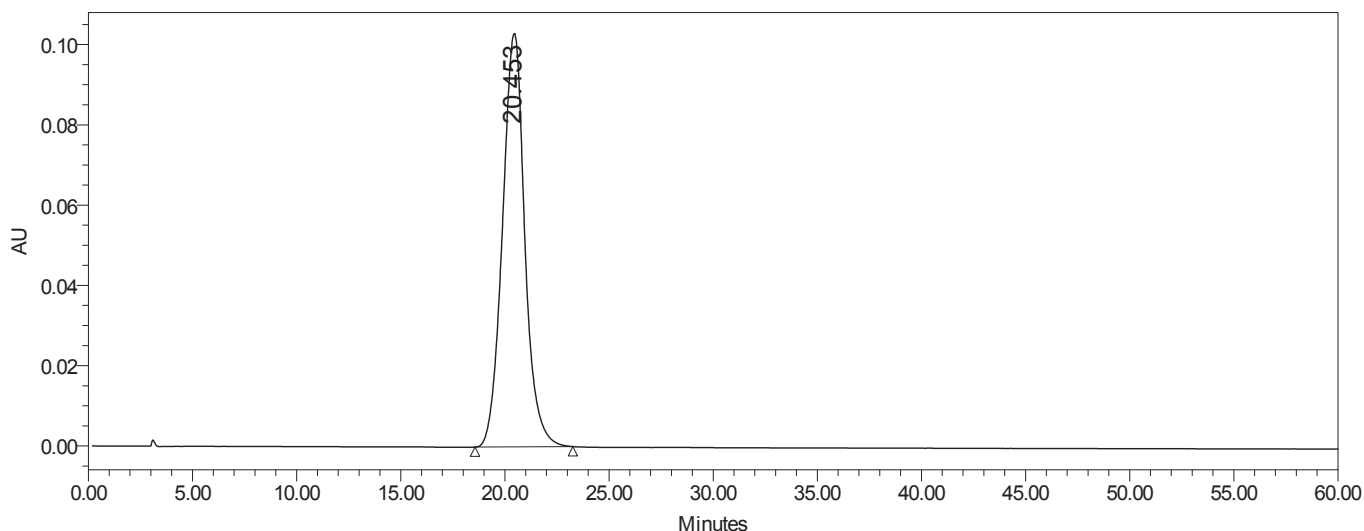
	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	20.361	5051245	49.90	67264
2	W2489 ChA 254nm	27.736	5071501	50.10	32698



Injection Summary Report

SAMPLE INFORMATION

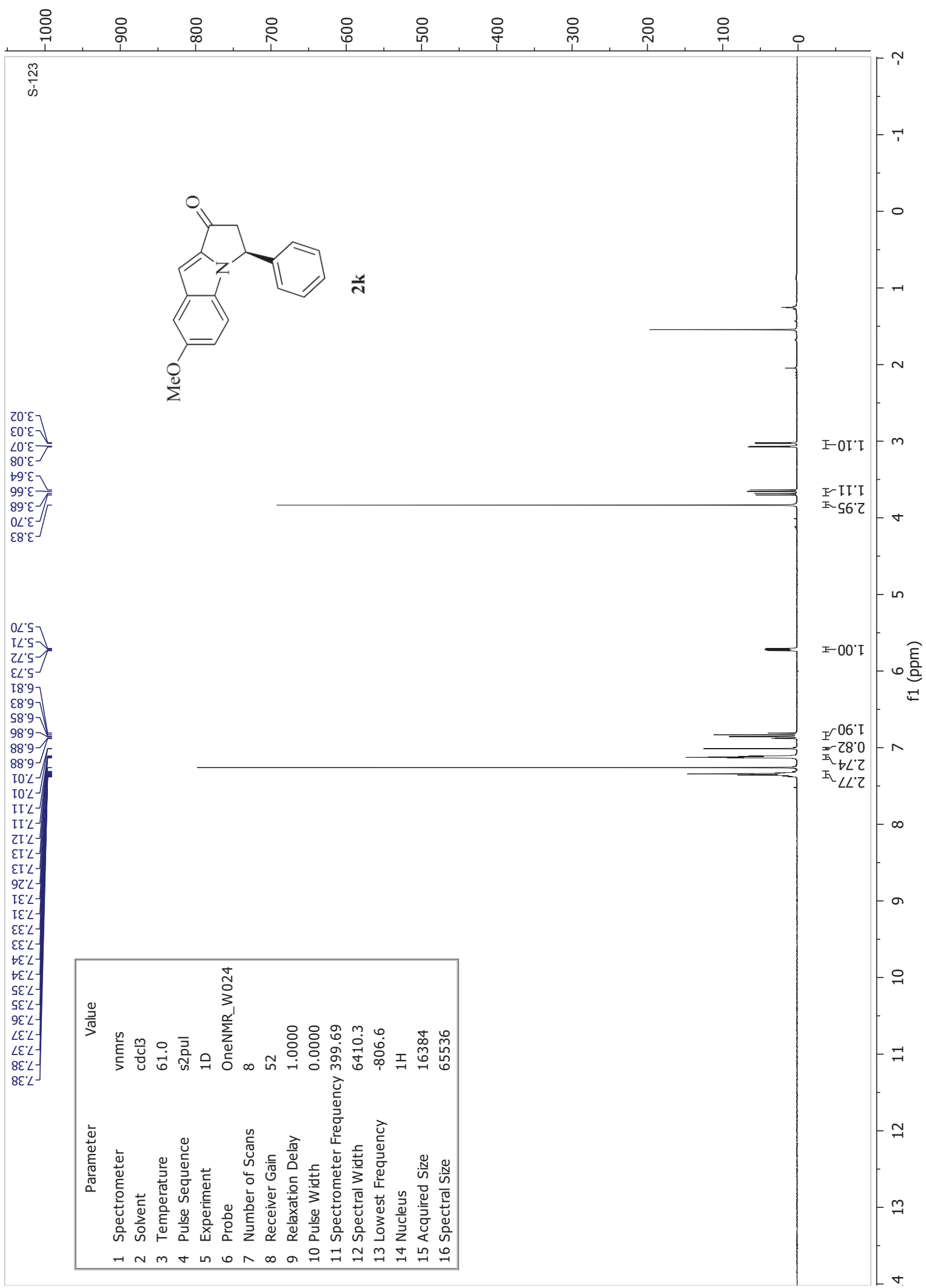
Sample Name:	avi_108_adh_95_5_1mpm	Acquired By:	System
Sample Type:	Unknown	Sample Set Name	avi_sep_3_2013
Vial:	21	Acq. Method Set:	1_ADH 95_5 1mpm
Injection #:	1	Processing Method	avi_109
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	60.0 Minutes	Proc. Chnl. Descr.:	W2489 ChA 254nm
Date Acquired:	9/3/2013 4:56:29 PM CDT		
Date Processed:	9/3/2013 8:04:05 PM CDT		



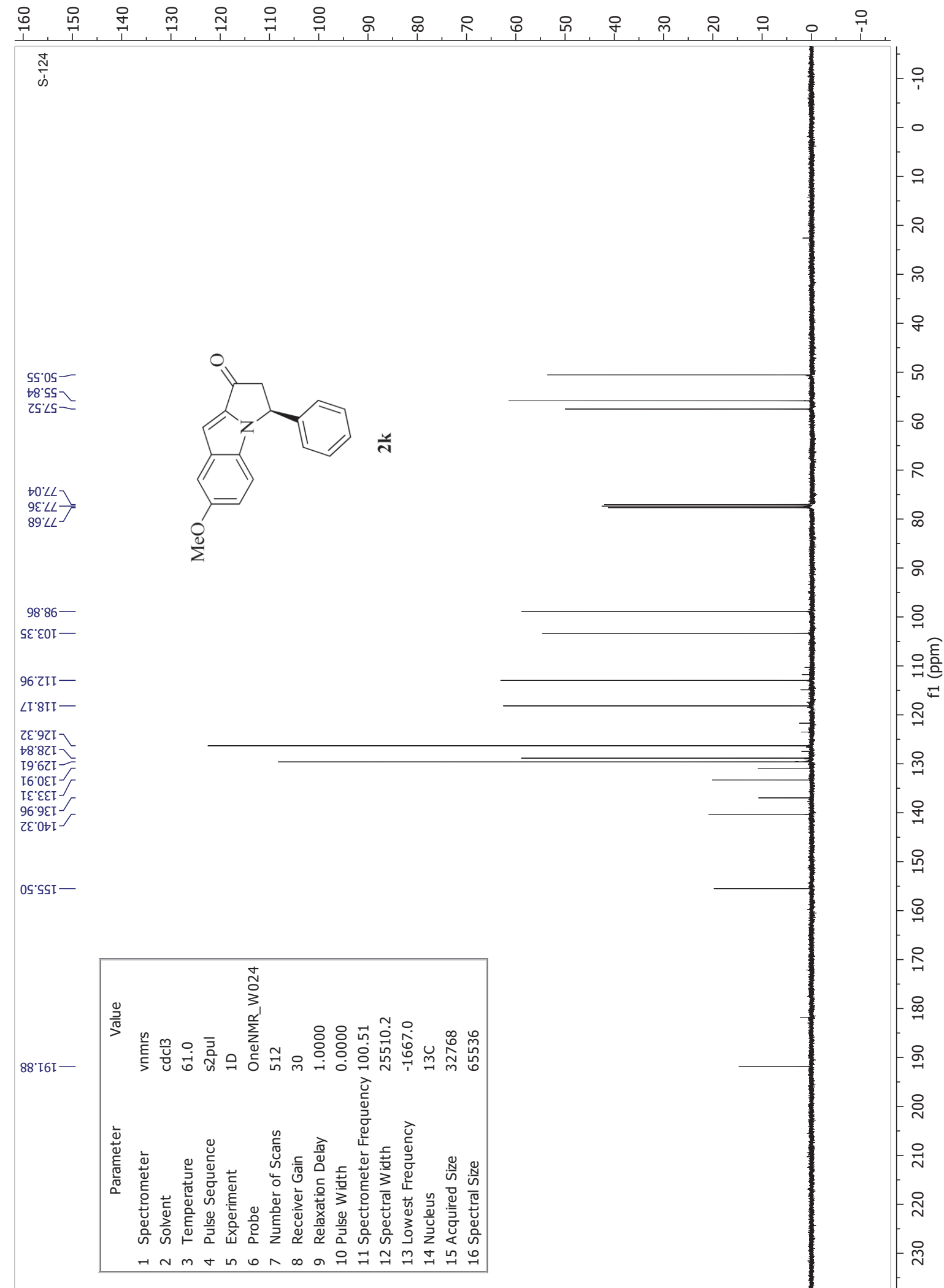
Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 6040; Processing Method: avi_109

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	20.453	7674250	100.00	102998



Parameter	Value
1 Spectrometer	vnmr5
2 Solvent	cdcl3
3 Temperature	61.0
4 Pulse Sequence	s2pul
5 Experiment	1D
6 Probe	OneNMR_W024
7 Number of Scans	8
8 Receiver Gain	52
9 Relaxation Delay	1.0000
10 Pulse Width	0.0000
11 Spectrometer Frequency	399.69
12 Spectral Width	6410.3
13 Lowest Frequency	-806.6
14 Nucleus	1H
15 Acquired Size	16384
16 Spectral Size	65536

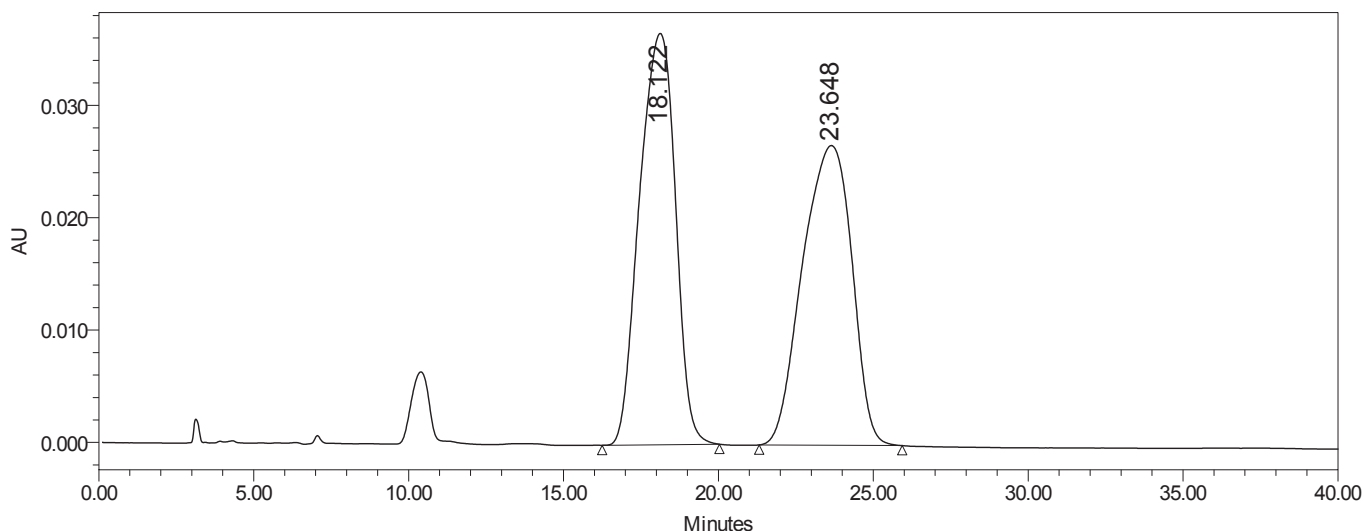




Injection Summary Report

SAMPLE INFORMATION

Sample Name:	AVI_adh95:5_1mpm_168	Acquired By:	System
Sample Type:	Unknown	Sample Set Name	
Vial:	44	Acq. Method Set:	1_ADH 95_5 1mpm
Injection #:	1	Processing Method	168
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	40.0 Minutes	Proc. Chnl. Descr.:	W2489 ChA 254nm
Date Acquired:	12/2/2012 6:47:13 PM CST		
Date Processed:	9/24/2013 10:12:32 PM CDT		



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 6813; Processing Method: 168

Processed Channel Descr.: W2489 ChA 254nm

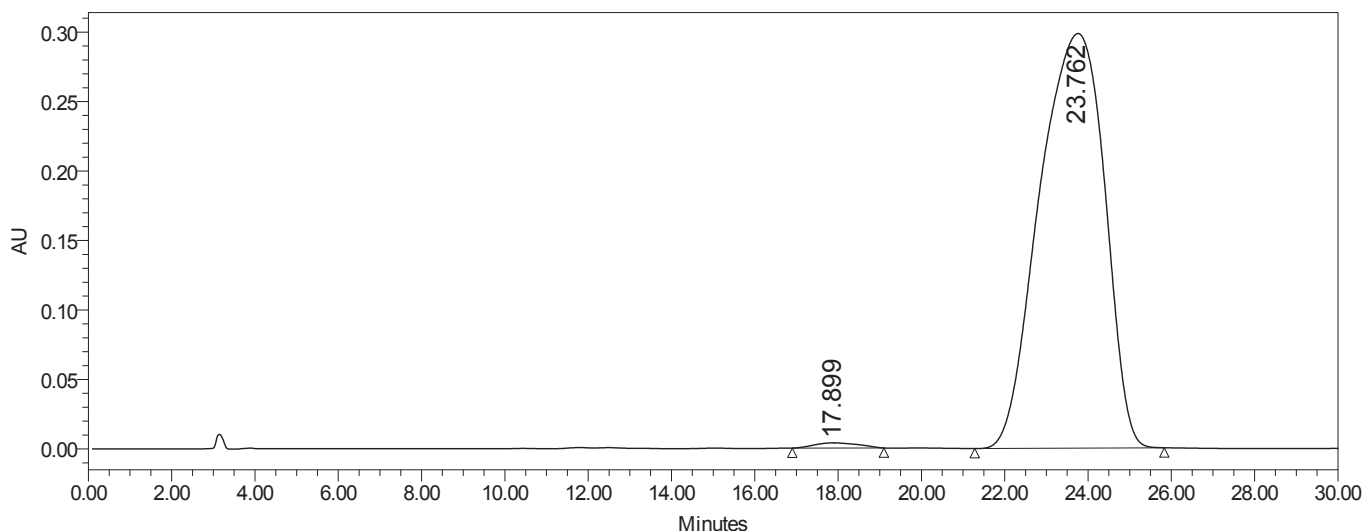
	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	18.122	2952026	50.00	36611
2	W2489 ChA 254nm	23.648	2951686	50.00	26681



Injection Summary Report

SAMPLE INFORMATION

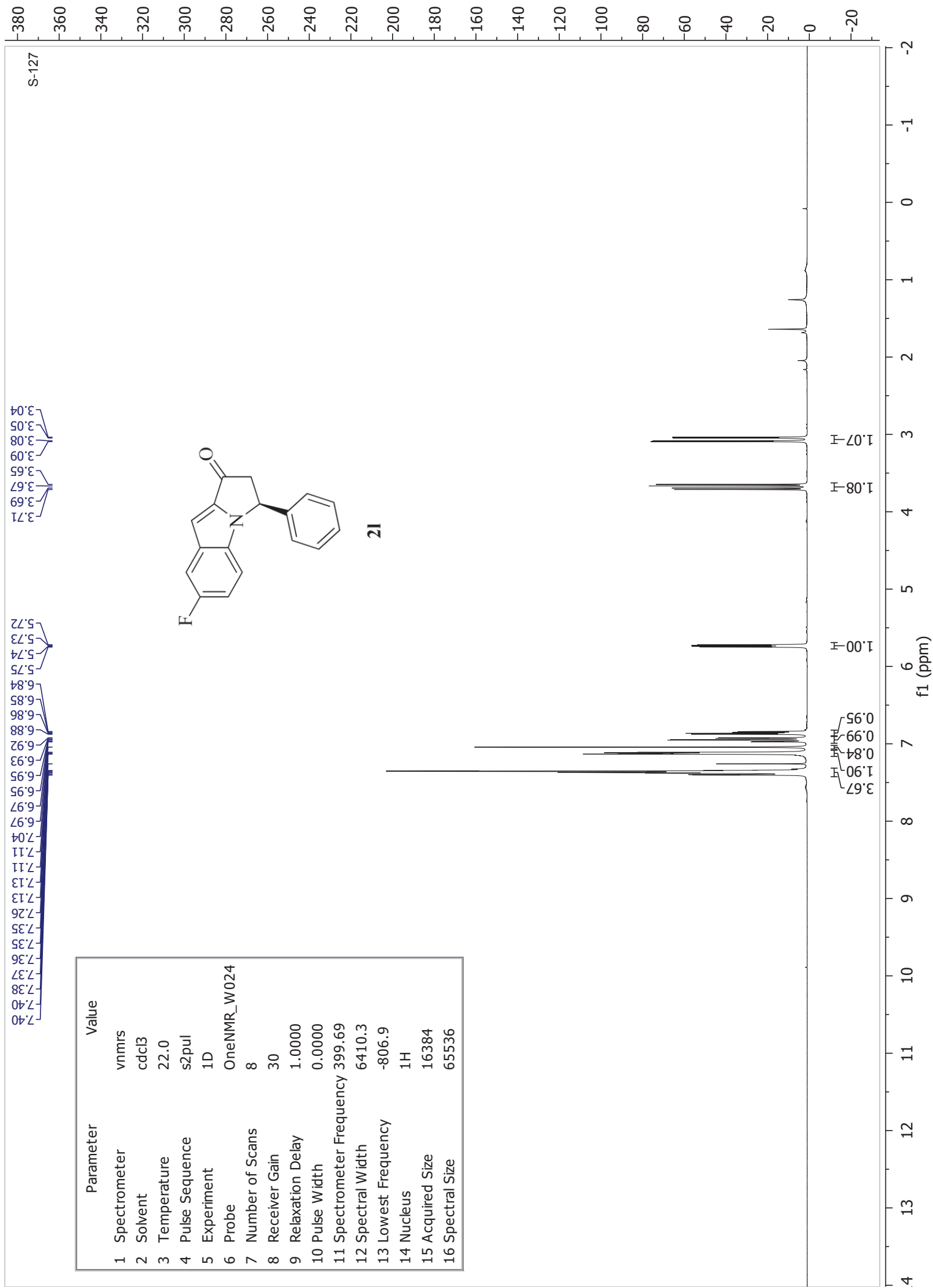
Sample Name:	AVI_adh95:5_1mpm_163	Acquired By:	System
Sample Type:	Unknown	Sample Set Name	
Vial:	64	Acq. Method Set:	1_ADH 95_5 1mpm
Injection #:	1	Processing Method	163
Injection Volume:	10.00 ul	Channel Name:	W2489 ChB
Run Time:	30.0 Minutes	Proc. Chnl. Descr.:	W2489 ChB 220nm
Date Acquired:	12/2/2012 8:26:57 PM CST		
Date Processed:	9/24/2013 10:16:15 PM CDT		

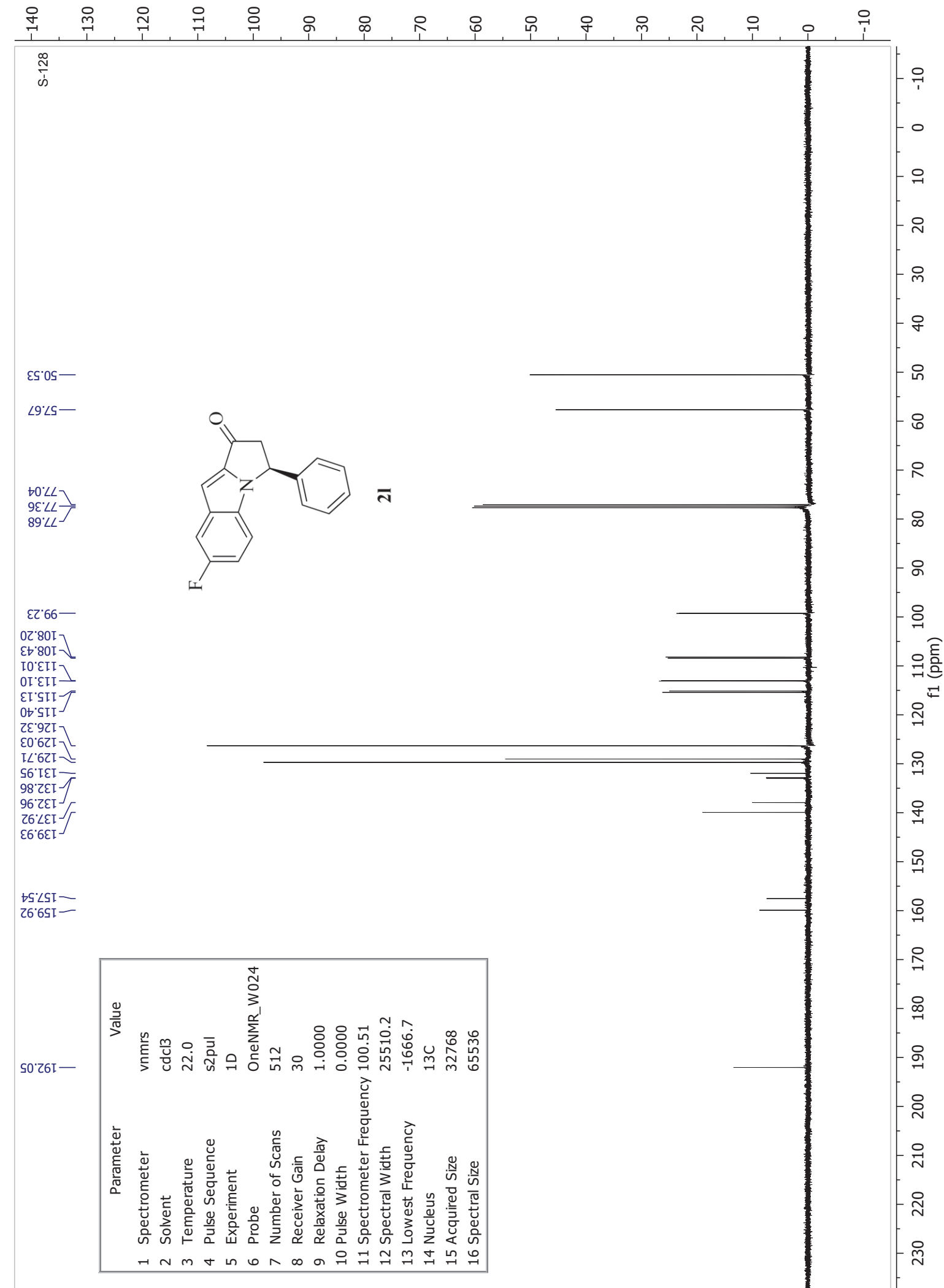


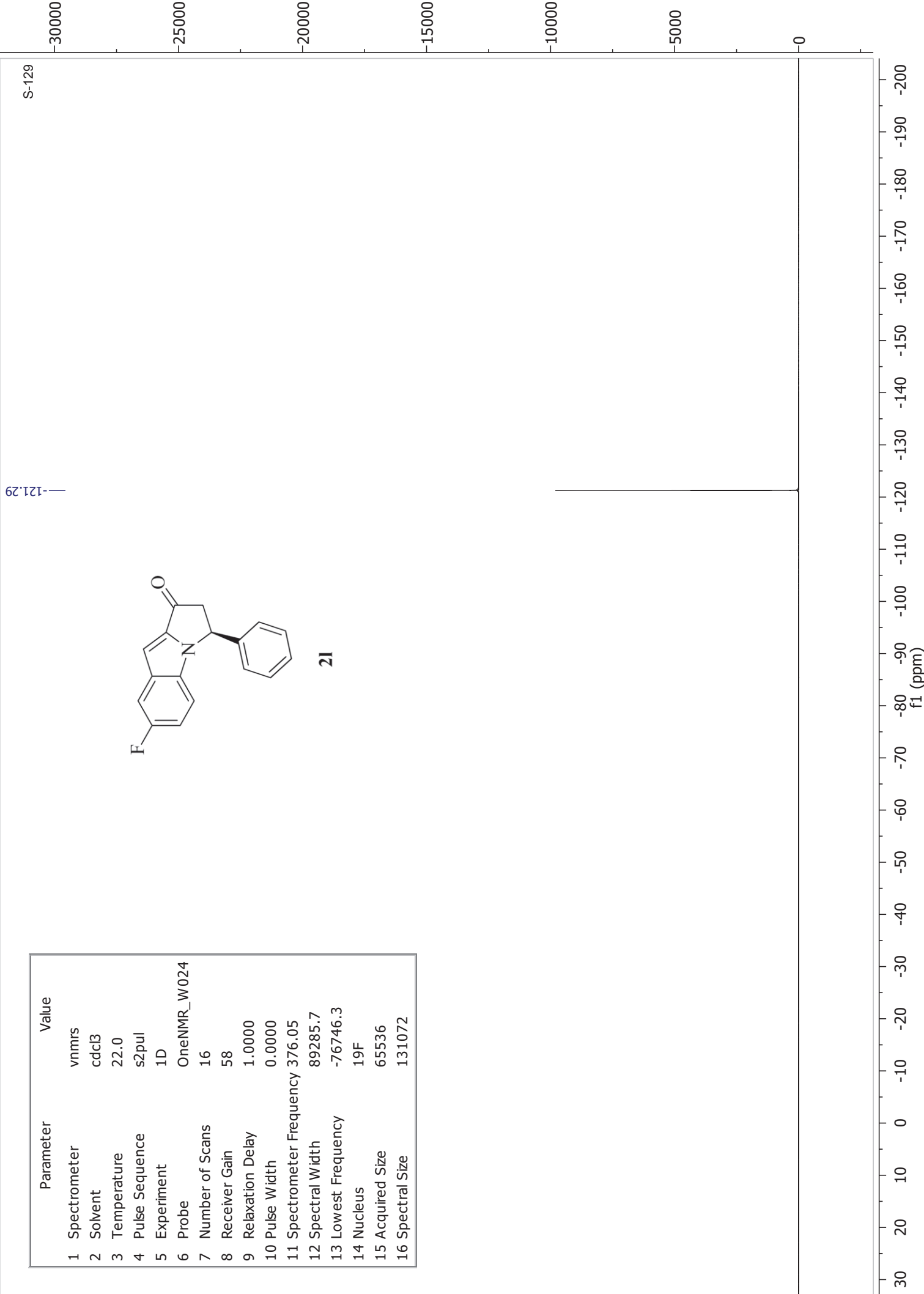
Channel: W2489 ChB; Processed Channel: W2489 ChB 220nm; Result Id: 6815; Processing Method: 163

Processed Channel Descr.: W2489 ChB 220nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 220nm	17.899	274957	0.84	3735
2	W2489 ChB 220nm	23.762	32468152	99.16	298468





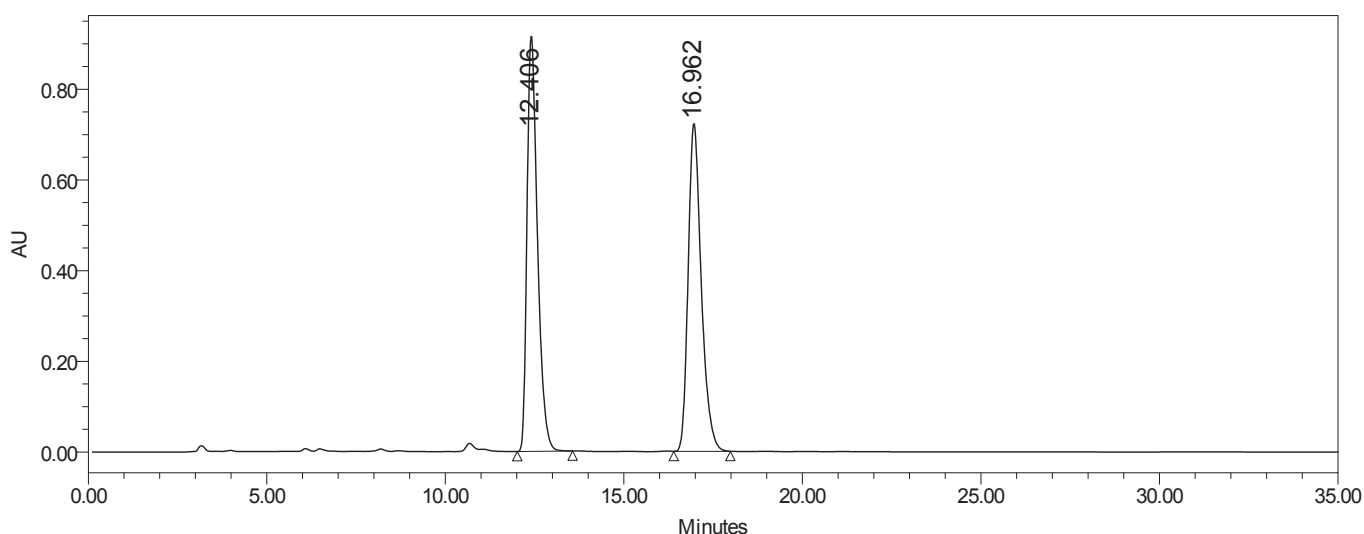




Injection Summary Report

SAMPLE INFORMATION

Sample Name:		Acquired By:	System
Sample Type:	Unknown	Sample Set Name	
Vial:	40	Acq. Method Set:	1_ADH 95_5 1mpm
Injection #:	1	Processing Method	177
Injection Volume:	10.00 ul	Channel Name:	W2489 ChB
Run Time:	35.0 Minutes	Proc. Chnl. Descr.:	W2489 ChB 220nm
Date Acquired:	12/10/2012 5:12:40 PM CST		
Date Processed:	9/24/2013 10:17:57 PM CDT		



Channel: W2489 ChB; Processed Channel: W2489 ChB 220nm; Result Id: 6817; Processing Method: 177

Processed Channel Descr.: W2489 ChB 220nm

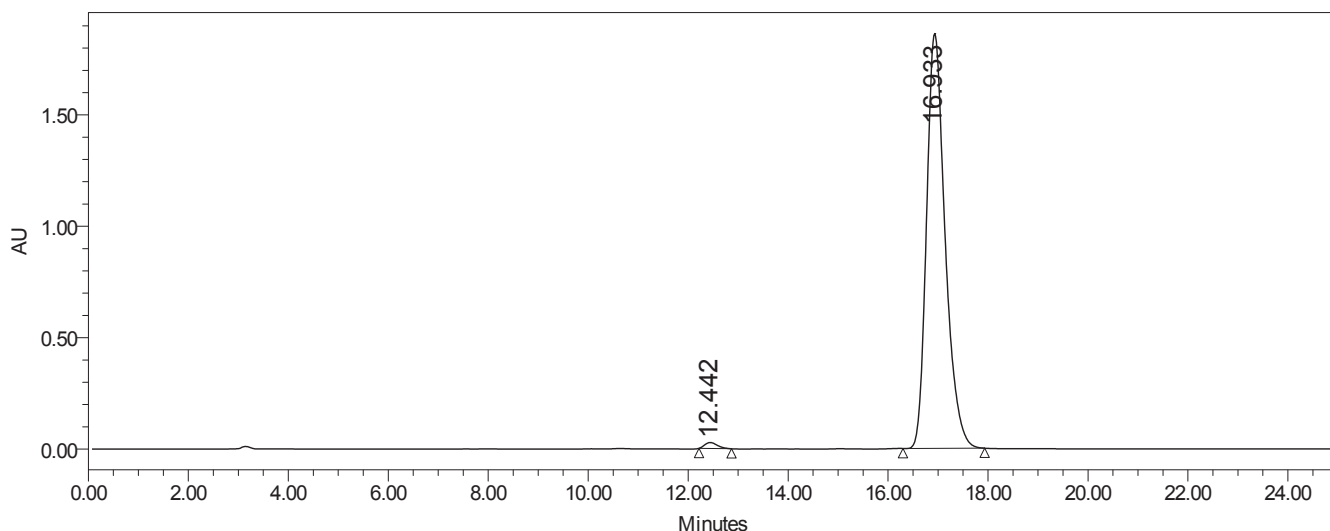
	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 220nm	12.406	18580818	50.14	916078
2	W2489 ChB 220nm	16.962	18479750	49.86	722244



Injection Summary Report

SAMPLE INFORMATION

Sample Name:		Acquired By:	System
Sample Type:	Unknown	Sample Set Name	
Vial:	50	Acq. Method Set:	1_ADH 95_5 1mpm
Injection #:	1	Processing Method	176
Injection Volume:	10.00 ul	Channel Name:	W2489 ChB
Run Time:	25.0 Minutes	Proc. Chnl. Descr.:	W2489 ChB 220nm
Date Acquired:	12/10/2012 6:23:17 PM CST		
Date Processed:	9/24/2013 10:19:01 PM CDT		

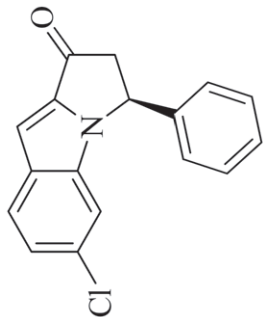


Channel: W2489 ChB; Processed Channel: W2489 ChB 220nm; Result Id: 6819; Processing Method: 176

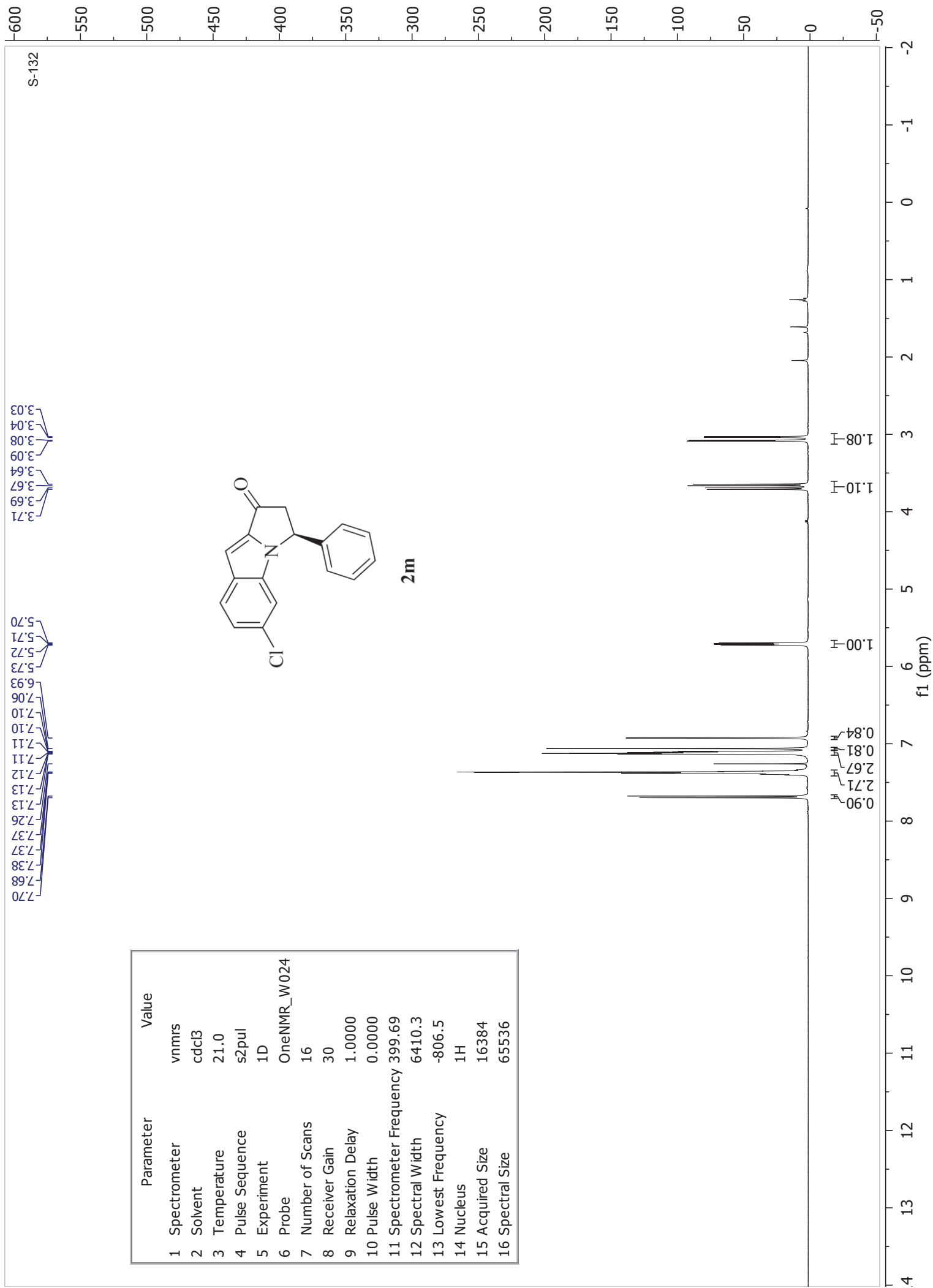
Processed Channel Descr.: W2489 ChB 220nm

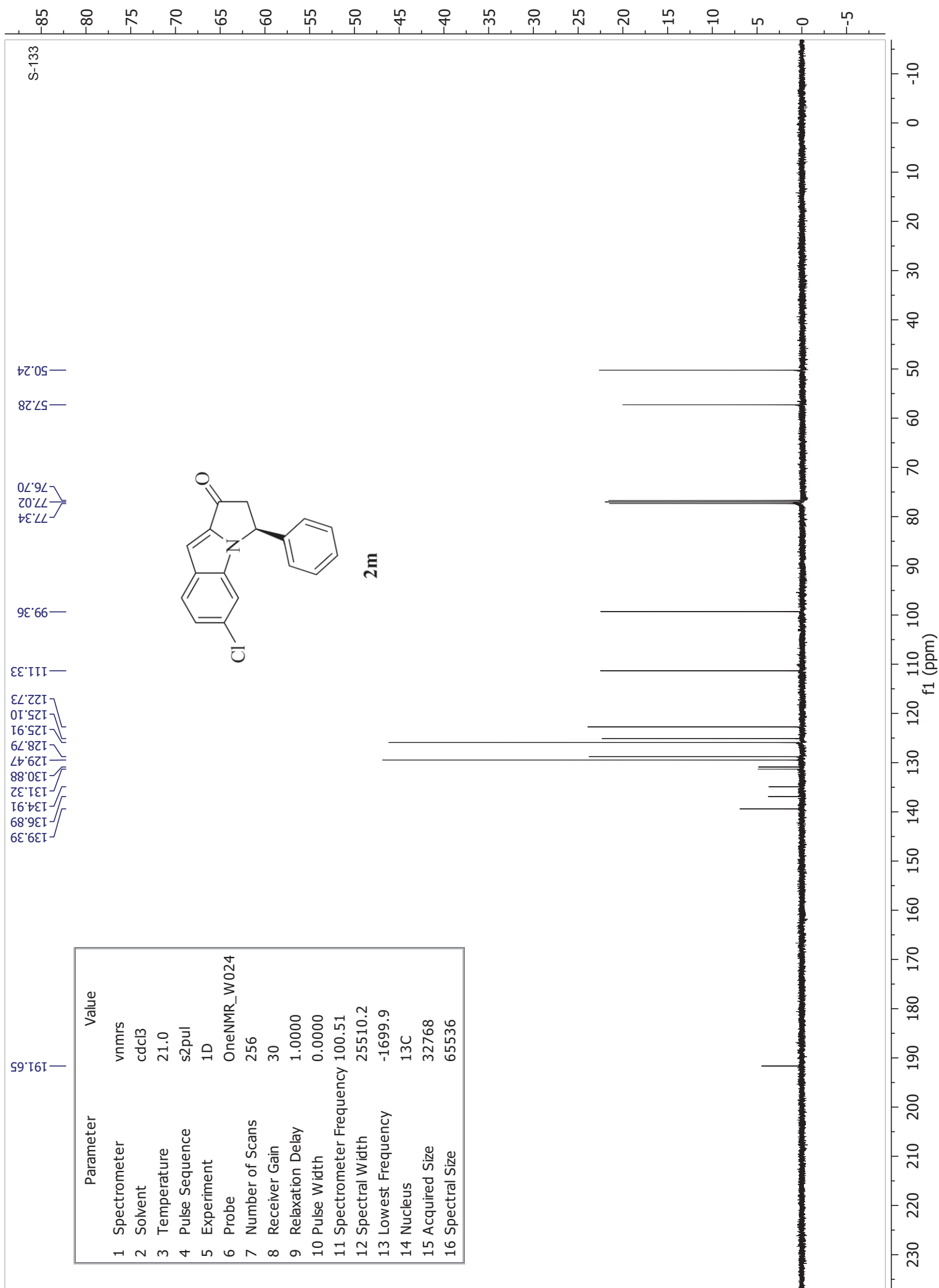
	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 220nm	12.442	466723	0.96	26689
2	W2489 ChB 220nm	16.933	48028403	99.04	1862235

Parameter	Value
1 Spectrometer	vnmr5
2 Solvent	cdcl3
3 Temperature	21.0
4 Pulse Sequence	s2pul
5 Experiment	1D
6 Probe	OneNMR_W024
7 Number of Scans	16
8 Receiver Gain	30
9 Relaxation Delay	1.0000
10 Pulse Width	0.0000
11 Spectrometer Frequency	399.69
12 Spectral Width	6410.3
13 Lowest Frequency	-806.5
14 Nucleus	¹ H
15 Acquired Size	16384
16 Spectral Size	65536



2m



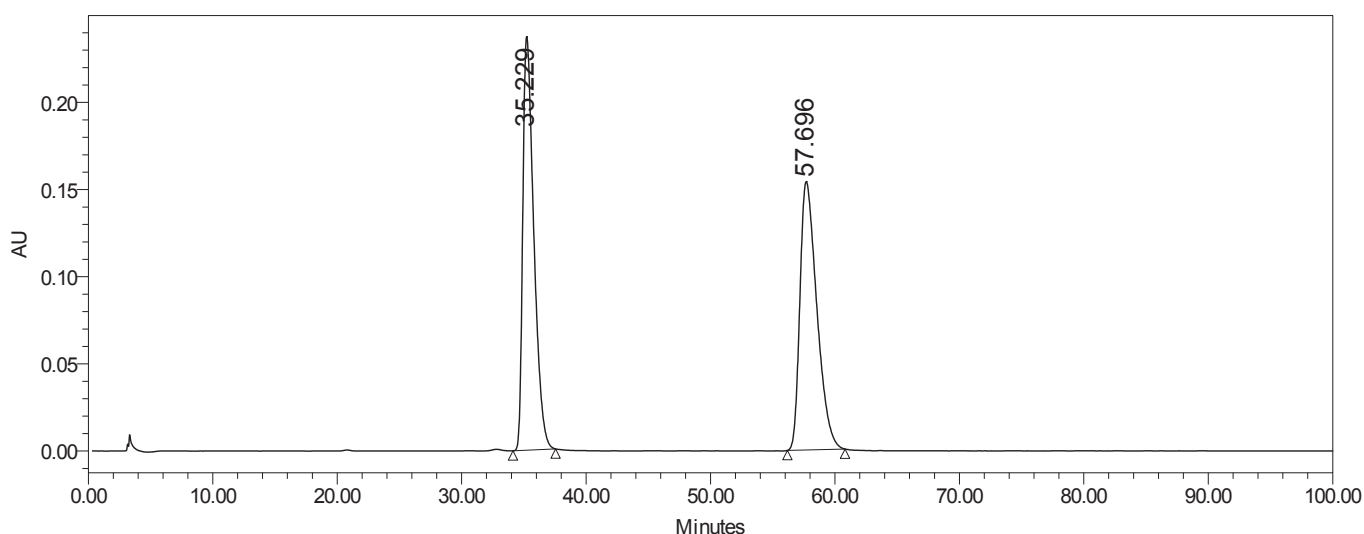




Injection Summary Report

SAMPLE INFORMATION

Sample Name:	nb_02_102_adh_99_1	Acquired By:	System
Sample Type:	Unknown	Sample Set Name	avi_mar31_2_2013
Vial:	19	Acq. Method Set:	1_ADH 99_1 1mpm
Injection #:	1	Processing Method	102
Injection Volume:	10.00 ul	Channel Name:	W2489 ChB
Run Time:	100.0 Minutes	Proc. Chnl. Descr.:	W2489 ChB 220nm
Date Acquired:	4/1/2013 1:35:51 AM CDT		
Date Processed:	9/9/2013 6:41:40 PM CDT		



Channel: W2489 ChB; Processed Channel: W2489 ChB 220nm; Result Id: 6267; Processing Method: 102

Processed Channel Descr.: W2489 ChB 220nm

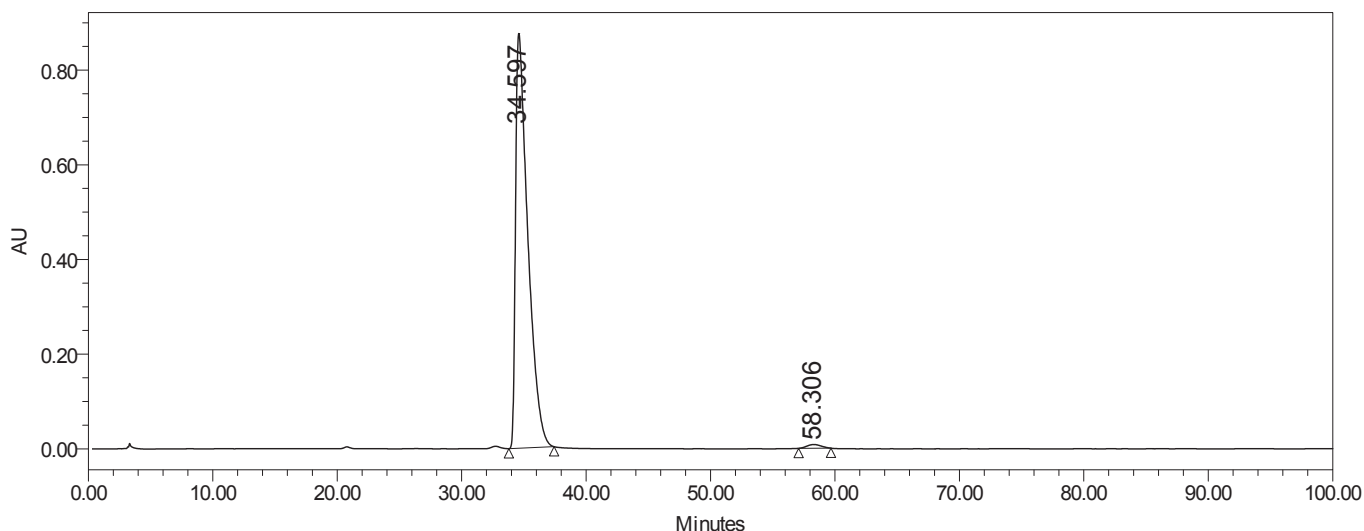
	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 220nm	35.229	14568311	50.08	237394
2	W2489 ChB 220nm	57.696	14522441	49.92	154060



Injection Summary Report

SAMPLE INFORMATION

Sample Name:	nb_02_101_adh_99_1	Acquired By:	System
Sample Type:	Unknown	Sample Set Name	avi_mar31_2_2013
Vial:	101	Acq. Method Set:	1_ADH 99_1 1mpm
Injection #:	1	Processing Method	101
Injection Volume:	10.00 ul	Channel Name:	W2489 ChB
Run Time:	100.0 Minutes	Proc. Chnl. Descr.:	W2489 ChB 220nm
Date Acquired:	4/1/2013 3:46:54 AM CDT		
Date Processed:	9/9/2013 6:44:13 PM CDT		

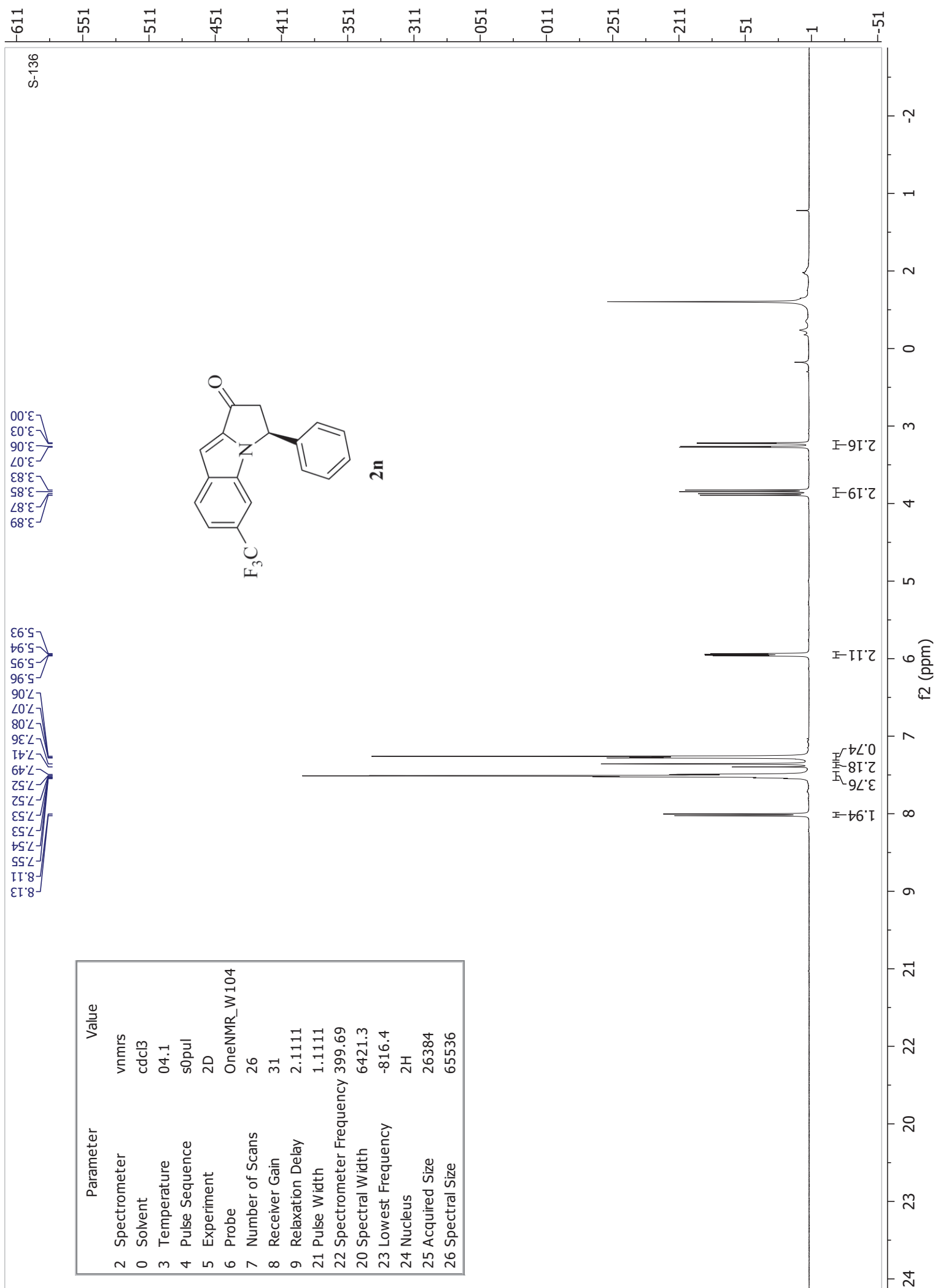


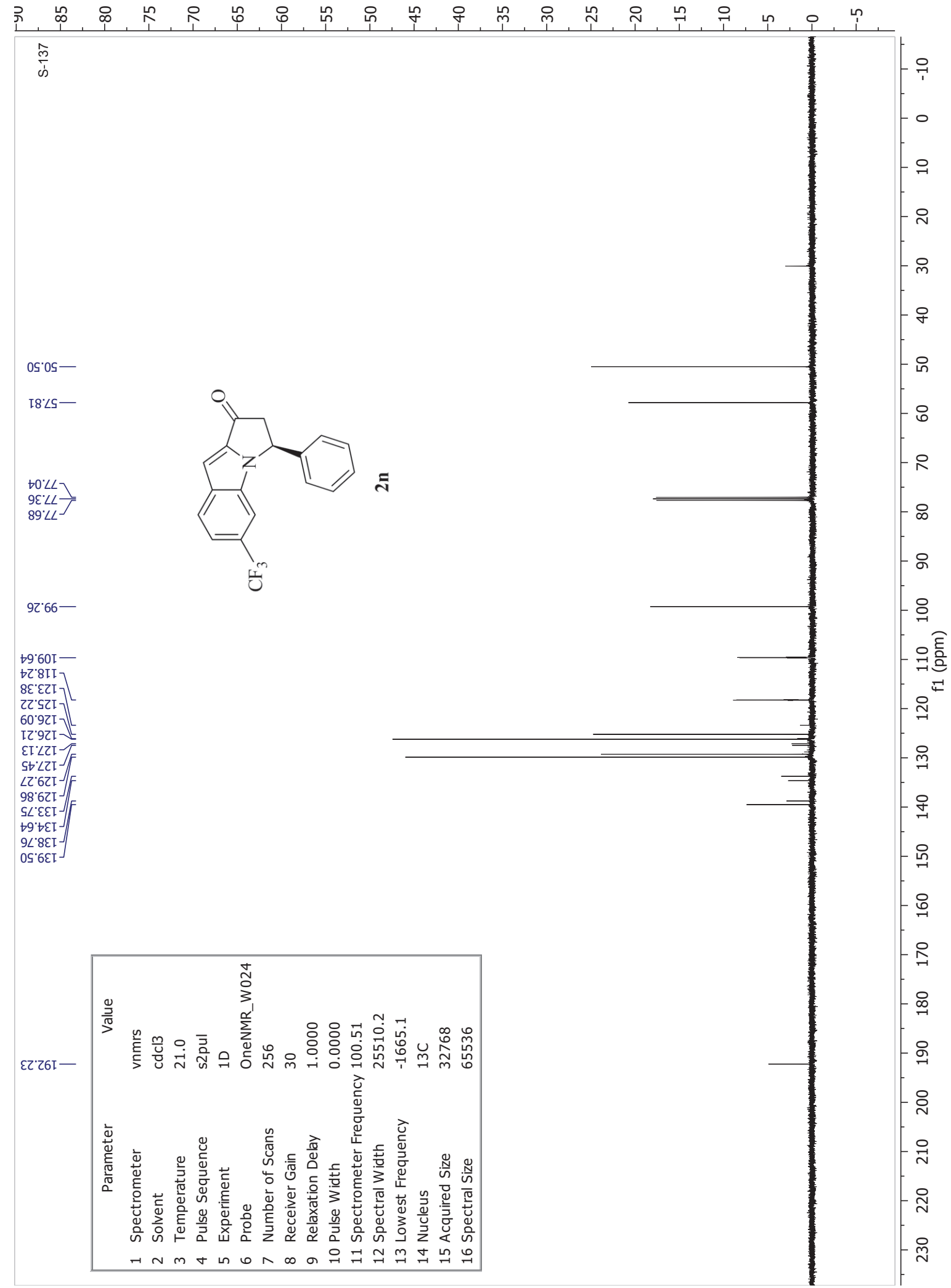
Channel: W2489 ChB; Processed Channel: W2489 ChB 220nm; Result Id: 6269; Processing Method: 101

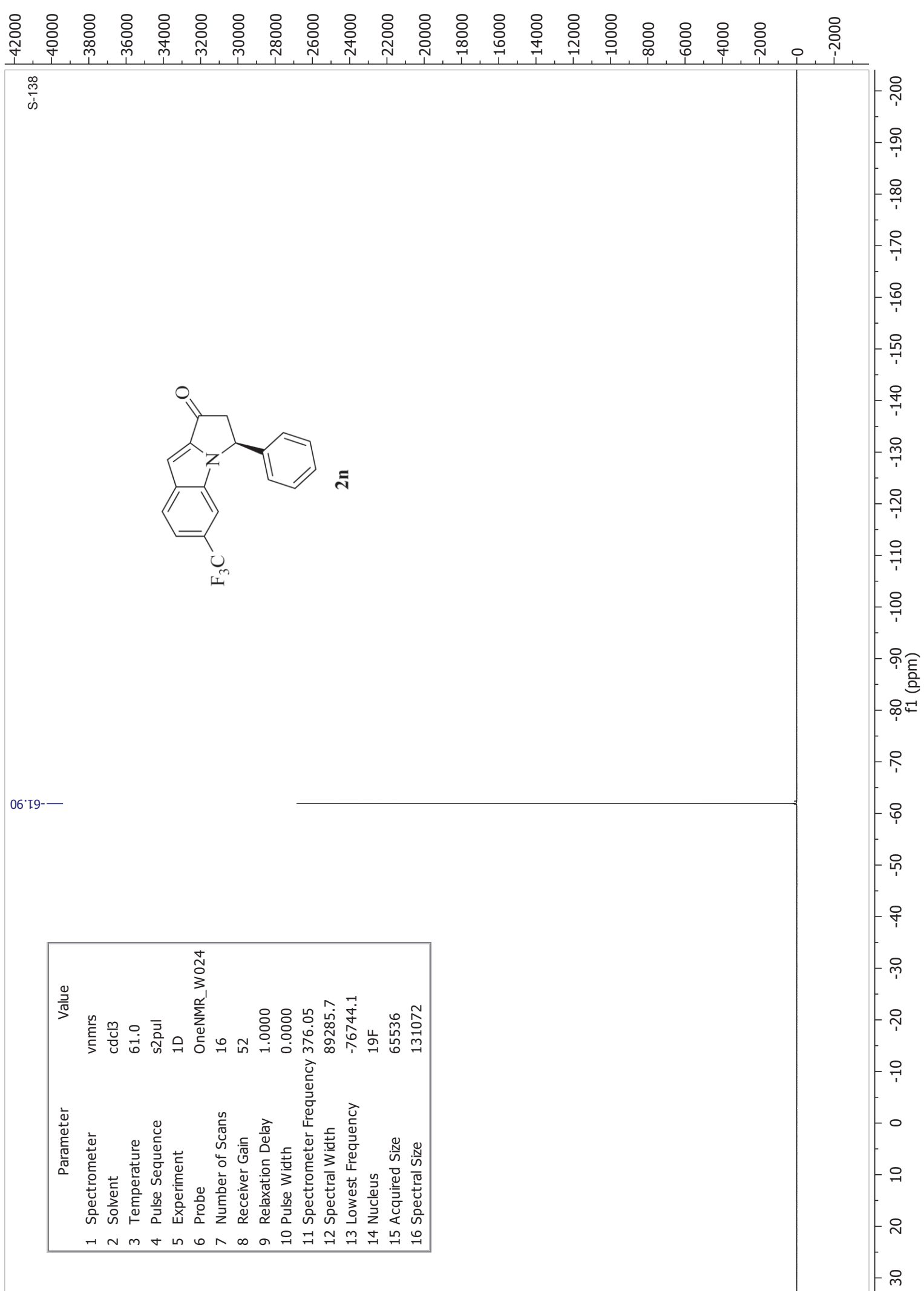
Processed Channel Descr.: W2489 ChB 220nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 220nm	34.597	59841484	98.97	876109
2	W2489 ChB 220nm	58.306	623060	1.03	7837

Parameter	Value
2 Spectrometer	vmrns
0 Solvent	cdc13
3 Temperature	04.1
4 Pulse Sequence	sOpul
5 Experiment	2D
6 Probe	OneNMR_W104
7 Number of Scans	26
8 Receiver Gain	31
9 Relaxation Delay	2.1111
21 Pulse Width	1.1111
22 Spectrometer Frequency	399.69
20 Spectral Width	6421.3
23 Lowest Frequency	-816.4
24 Nucleus	2H
25 Acquired Size	26384
26 Spectral Size	65536





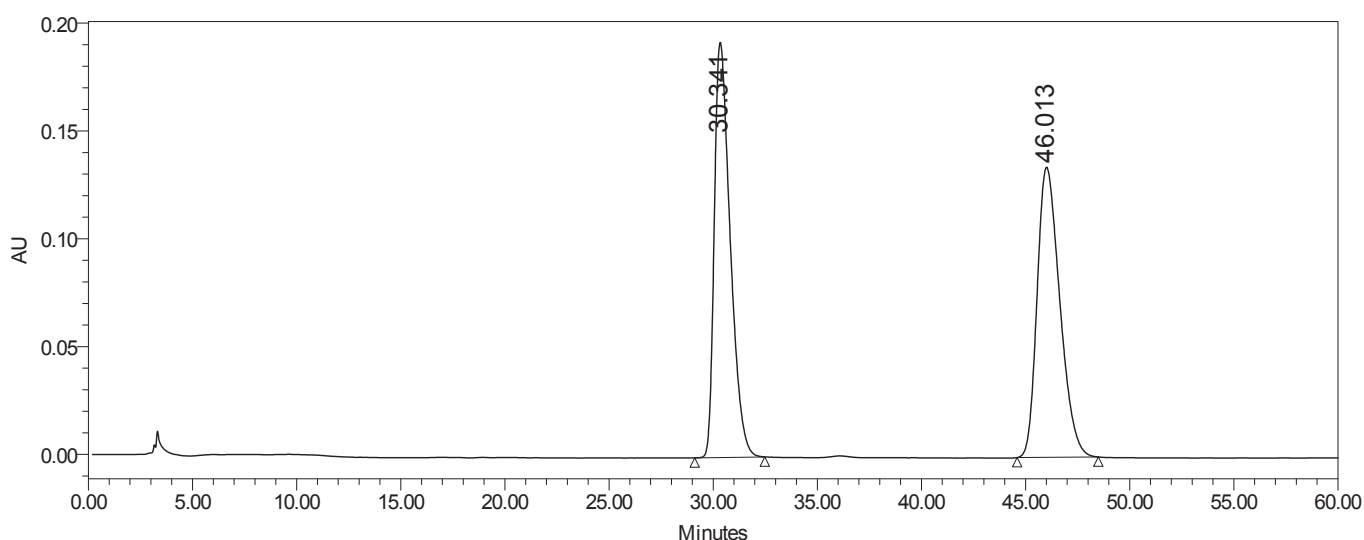




Injection Summary Report

SAMPLE INFORMATION

Sample Name:	nb_02_100_adh_99_1	Acquired By:	System
Sample Type:	Unknown	Sample Set Name	avi_mar31_2_2013
Vial:	18	Acq. Method Set:	1_ADH 99_1 1mpm
Injection #:	1	Processing Method	100
Injection Volume:	10.00 ul	Channel Name:	W2489 ChB
Run Time:	60.0 Minutes	Proc. Chnl. Descr.:	W2489 ChB 220nm
Date Acquired: 3/31/2013 10:33:50 PM CDT			
Date Processed: 9/9/2013 6:47:09 PM CDT			



Channel: W2489 ChB; Processed Channel: W2489 ChB 220nm; Result Id: 6271; Processing Method: 100

Processed Channel Descr.: W2489 ChB 220nm

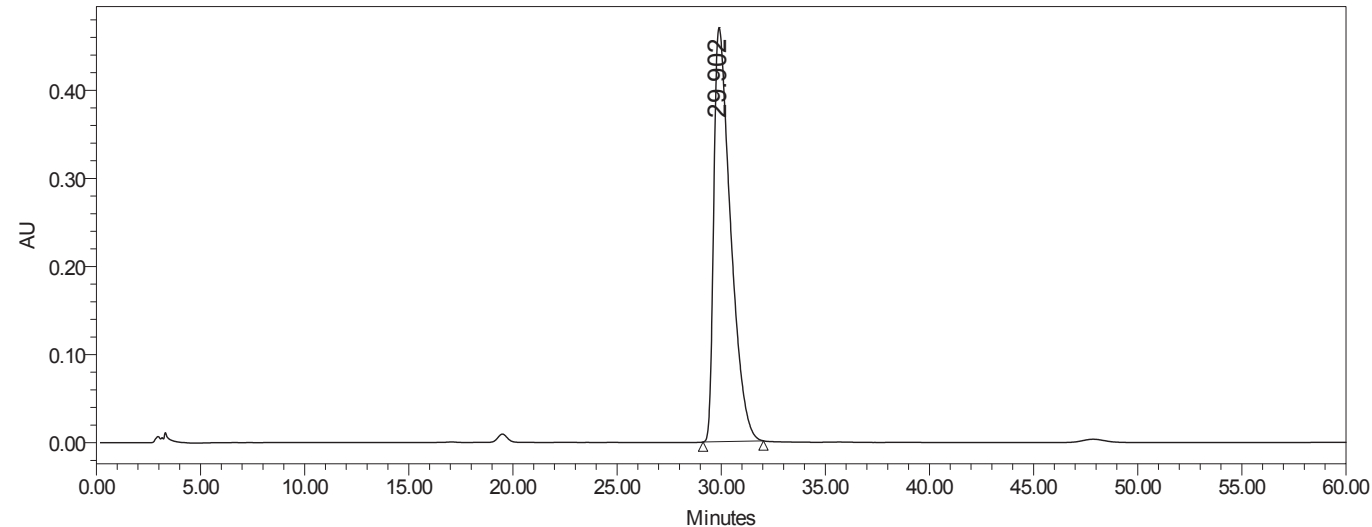
	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 220nm	30.341	10211541	50.08	192519
2	W2489 ChB 220nm	46.013	10180068	49.92	134540



Injection Summary Report

SAMPLE INFORMATION

Sample Name:	nb_02_99_adh_99_1	Acquired By:	System
Sample Type:	Unknown	Sample Set Name	avi_mar31_2_2013
Vial:	99	Acq. Method Set:	1_ADH 99_1 1mpm
Injection #:	1	Processing Method	99
Injection Volume:	10.00 ul	Channel Name:	W2489 ChB
Run Time:	60.0 Minutes	Proc. Chnl. Descr.:	W2489 ChB 220nm
Date Acquired:	4/1/2013 12:04:48 AM CDT		
Date Processed:	9/9/2013 6:49:00 PM CDT		



Channel: W2489 ChB; Processed Channel: W2489 ChB 220nm; Result Id: 6273; Processing Method: 99

Processed Channel Descr.: W2489 ChB 220nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 220nm	29.902	26276467	100.00	470199

