

Formation of Medium-Sized Nitrogen Heterocycles from γ -Silyloxy- γ -Lactams

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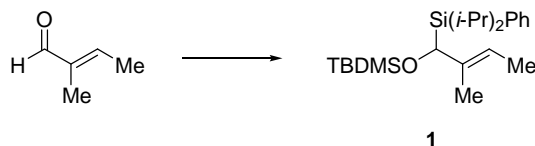
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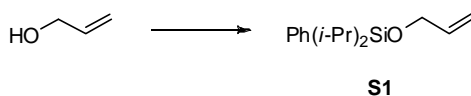
General. ^1H NMR and ^{13}C NMR spectra were recorded at ambient temperature at 500 and 125 MHz, respectively. The data are reported as follows: chemical shift in ppm from internal tetramethylsilane on δ scale, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), and integration. High resolution mass spectra were acquired by peak matching. Analytical gas-liquid chromatography (GLC) was performed on a gas chromatograph equipped with an auto sampler and a flame ionization detector. A fused silica, wall-coated capillary column (30 m x 0.32 mm x 0.25 μm) was used with helium as the carrier gas. Melting points were obtained using a melting point apparatus and were reported uncorrected. Liquid chromatography was performed using forced flow (flash chromatography) of the indicated solvent system on 60 (230–400) mesh silica gel (SiO_2). All reactions, unless specified, were performed under an atmosphere of nitrogen in glassware that had been flame-dried under vacuum. Unless otherwise noted, all reagents were commercially obtained, and where appropriate, purified prior to use. Toluene, THF, Et_2O , and CH_2Cl_2 were dried by filtration through alumina according to the procedure of Grubbs.¹ $\text{BF}_3\cdot\text{OEt}_2$ was distilled from Et_2O and stored in a sealed tube. Alkylolithium reagents were purchased and titrated prior to use with *N*-benzylbenzamide.² Silyllithium reagents were prepared and titrated according to the procedure of Fleming.^{3,4}

I. Synthesis of α -Silyloxy Allylic Silanes

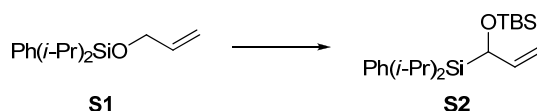


α -Siloxy Allylic Silane 1. To a solution of $\text{PhLi-Pr}_2\text{SiCl}$ ⁵ (8.43 g, 37.0 mmol) in THF (75 mL) was added lithium wire (1.30 g, 185 mmol). The suspension was stirred at 24 °C for 18 h. The resultant red solution was transferred to a dry flask and cooled to –78 °C as a solution of *trans*-2-methyl-2-butenal (3.00 mL, 31.0 mmol) in THF (50 mL) was added dropwise. The reaction mixture was stirred at –78 °C for 2 h. The reaction mixture was diluted with saturated aqueous NH_4Cl (100 mL). The layers were separated and the aqueous layer was extracted with EtOAc (3 \times 50 mL). The combined organic layers were washed with saturated aqueous NaCl (100 mL). The resultant organic phase was dried with MgSO_4 and filtered. The filtrate was concentrated *in vacuo* to afford a yellow oil. The oil was dissolved in DMF (10 mL) and TBDMSCl (9.35 g, 62.0 mmol) and imidazole (3.17 g, 46.5 mmol) were added. The reaction mixture was stirred at 24 °C for 18 h. The reaction mixture was diluted with saturated aqueous NH_4Cl (100 mL) and hexanes (50 mL). The layers were separated and the aqueous layer was extracted with hexanes (3 \times 75 mL). The combined organic layers were washed with saturated aqueous NaCl (75 mL). The resultant organic phase was dried with MgSO_4 and filtered. The filtrate was concentrated *in vacuo* to afford unpurified **1** as a colorless oil. Purification by flash chromatography (hexanes) provided **1** as a colorless oil (8.82 g, 73%): ^1H NMR (CDCl_3 , 400 MHz) δ 7.63 (m, 2H), 7.30 (m, 3H), 5.35 (q, J = 6.7, 1H), 4.36 (s, 1H), 1.52 (d, J = 6.8, 3H), 1.44–1.33 (m, 2H), 1.39 (s, 3H), 1.12 (m, 9H), 1.01 (d, J = 7.5, 3H), 0.88 (s, 9H), 0.02 (s, 3H), –0.06 (s, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 138.1, 135.9, 135.5, 128.8, 127.3, 119.4, 72.7, 26.2, 18.9, 18.7, 18.6, 18.5, 18.4, 14.6, 13.4, 11.7, 11.0, –3.8, –

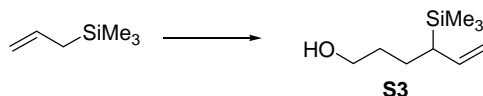
5.2; IR (thin film) 2929, 2865, 1465, 1254 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{23}\text{H}_{43}\text{OSi}_2$ ($M + H$)⁺ 391.2852, found 391.2845. Anal. Calcd for $\text{C}_{23}\text{H}_{42}\text{OSi}_2$: C, 70.70; H, 10.83. Found: C, 70.98; H, 10.99.



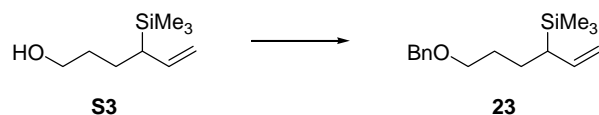
Allylic Silylether S1. To a solution of allylic alcohol (1.70 mL, 25.0 mmol), $\text{Ph}(\text{i-Pr})_2\text{SiCl}_5$ (6.24 g, 27.5 mmol), and DMAP (0.611 g, 5.00 mmol) in CH_2Cl_2 (50 mL) was added a solution of triethylamine (4.20 mL, 30.0 mmol) in CH_2Cl_2 (10 mL). The reaction mixture was stirred at 24 °C for 12 h. The reaction mixture was diluted with saturated aqueous NH_4Cl (50 mL) and concentrated *in vacuo*. Hexanes (30 mL) was added, and the layers were separated. The aqueous layer was extracted with hexanes (3×20 mL), and the combined organic layers were washed with saturated aqueous NaCl (50 mL). The resultant organic phase was dried with MgSO_4 and filtered. The filtrate was concentrated *in vacuo* to afford unpurified **S1** as a yellow oil. Purification by flash chromatography (hexanes to 10:90 EtOAc/hexanes) provided **S1** as a clear oil (5.38 g, 87%): ^1H NMR (CDCl_3 , 400 MHz) δ 7.55 (m, 2H), 7.37 (m, 3H), 6.03–5.93 (ddt, $J = 17.1, 10.5, 4.4$, 1H), 5.39 (ddd, $J = 17.1, 2.0, 2.0$, 1H), 5.14 (ddd, $J = 10.5, 1.8, 1.8$, 1H), 4.32 (ddd, $J = 4.4, 1.9, 1.9$, 2H), 1.34–1.26 (m, 2H), 1.08 (d, $J = 7.4$, 6H), 1.02 (d, $J = 7.5$, 6H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 137.4, 134.8, 134.3, 129.4, 127.8, 114.1, 64.8, 17.6, 17.4, 12.3; IR (thin film) 2944, 2867, 1465 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{15}\text{H}_{24}\text{NaOSi}$ ($M + \text{Na}$)⁺ 271.1494, found 271.1503. Anal. Calcd for $\text{C}_{15}\text{H}_{24}\text{OSi}$: C, 72.52; H, 9.74. Found: C, 72.63; H, 9.84.



Allylic Silane S2. To a cooled solution of **S1** (4.10 g, 16.5 mmol) and LiCl (2.10 g, 49.5 mmol) in THF (100 mL) was added *s*-BuLi (33.0 mL, 1.0 M in 92:8 cyclohexane/hexanes, 33 mmol). The reaction mixture was warmed to –42 °C, and stirred for 1 h. The reaction mixture was poured onto a vigorously stirring saturated solution of aqueous NH_4Cl (800 mL). The layers were separated, and the aqueous layer was extracted with EtOAc (3×100 mL). The combined organic layers were washed with saturated aqueous NaCl (75 mL). The resultant organic phase was dried with Na_2SO_4 and filtered. The filtrate was concentrated *in vacuo* to afford a yellow oil. The oil was dissolved in DMF (30 mL) and stirred at 24 °C as TBDMSCl (4.97 g, 33.0 mmol) and imidazole (1.68 g, 24.8 mmol) were added. The reaction mixture was stirred at 24 °C for 18 h. The reaction mixture was diluted with saturated aqueous NH_4Cl (100 mL) and hexanes (50 mL). The layers were separated and aqueous layer was extracted with hexanes (3×30 mL). The combined organic layers were washed with saturated aqueous NaCl (50 mL). The resultant organic phase was dried with MgSO_4 and filtered. The filtrate was concentrated *in vacuo* to afford unpurified **S2** as a colorless oil. Purification by flash chromatography (hexanes) provided **S2** as a colorless oil (4.66 g, 78%): ^1H NMR (CDCl_3 , 400 MHz) δ 7.54 (m, 2H), 7.31 (m, 3H), 5.96 (ddd, $J = 17.2, 10.5, 6.7$, 1H), 5.05 (dt, $J = 17.1, 1.8$, 1H), 4.89 (dt, $J = 10.5, 1.8$, 1H), 4.53 (dt, $J = 6.7, 1.7$, 1H), 1.47–1.35 (m, 2H), 1.10 (d, $J = 7.5$, 3H), 1.09 (d, $J = 7.5$, 6H), 1.08 (d, $J = 7.5$, 3H), 0.86 (s, 9H), –0.01 (s, 3H), –0.04 (s, 3H).



Alcohol S3. To a cooled (–42 °C) solution of allyltrimethylsilane (22.0 mL, 139 mmol) and *N,N,N',N'*-tetramethyl-ethane-1,2-diamine (20.9 mL, 139 mmol) in THF (300 mL) was added *s*-BuLi (104 mL, 1.33 M solution in hexanes, 139 mmol). After 30 min, 3-bromo-1-propanol (5.00 mL, 55.4 mmol) was added over 15 min by syringe pump. The reaction mixture was warmed to 24 °C and stirred for 12 h. The reaction mixture was diluted with Et_2O (100 mL) and saturated aqueous NaHCO_3 (100 mL). The layers were separated and the aqueous layer was extracted with Et_2O (3×50 mL). The combined organic layers were washed with saturated aqueous NaCl (100 mL). The resultant organic phase was dried with Na_2SO_4 and filtered. The filtrate was concentrated *in vacuo* to afford unpurified **S3** as a yellow oil. Purification by flash chromatography (10:90 to 30:70 EtOAc/hexanes) provided **S3** as a colorless oil (5.76 g, 60%). Spectral data was identical to that reported in literature:⁶ ^1H NMR (CDCl_3 , 400 MHz) δ 5.63 (ddd, $J = 17.1, 10.3, 9.2$, 1H), 4.91 (dd, $J = 10.3, 2.0$, 1H), 4.85 (ddd, $J = 17.0, 2.0, 0.9$, 1H), 3.66 (m, 2H), 1.74 (m, 1H), 1.63–1.41 (m, 4H), 0.00 (s, 9H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 140.2, 112.3, 63.1, 34.8, 32.7, 24.7, –1.0, –3.2; IR (thin film) 3309, 1627, 1248 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_9\text{H}_{20}\text{NaOSi}$ ($M + \text{Na}$)⁺ 195.1181, found 195.1180. Anal. Calcd for $\text{C}_9\text{H}_{20}\text{OSi}$: C, 62.72; H, 11.70. Found: C, 62.93; H, 11.86.

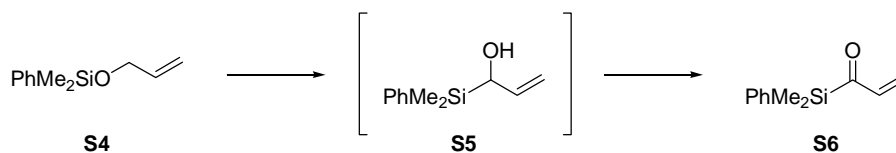


Allylic Silane 23. To a cooled (0 °C) suspension of NaH (0.059 g, 2.3 mmol) in THF (2 mL) was added a solution of **S3** (0.200 g, 1.16 mmol) in THF (2 mL). The reaction mixture was stirred at 0 °C for 30 min, and benzylbromide (0.28 mL, 2.3 mmol) was added dropwise. The reaction mixture was warmed to 24 °C and stirred for 20 h. The reaction mixture was diluted with EtOAc (10 mL) and saturated aqueous H₂O (10 mL). The layers were separated and the aqueous layer was extracted with EtOAc (3 × 5 mL). The combined organic layers were washed with saturated aqueous NaCl (10 mL). The resultant organic phase was dried with Na₂SO₄ and filtered. The filtrate was concentrated *in vacuo* to afford unpurified **23** as a colorless oil. Purification by flash chromatography (2:1 to 1:1 hexanes/toluene) provided **23** as a colorless oil (0.285 g, 94%): ¹H NMR (CDCl₃, 400 MHz) δ 7.35 (m, 4H), 7.28 (m, 1H), 5.60 (ddd, *J* = 17.1, 10.3, 9.3, 1H), 4.88 (dd, *J* = 10.3, 1.9, 1H), 4.80 (ddd, *J* = 17.1, 2.0, 0.9, 1H), 4.51 (s, 2H), 3.46 (t, *J* = 6.4, 2H), 1.79 (m, 1H), 1.68–1.35 (m, 4H), –0.03 (s, 9H); ¹³C NMR (CDCl₃, 125 MHz) δ 140.2, 138.8, 128.5, 127.8, 127.6, 112.2, 72.9, 70.3, 34.8, 29.5, 25.0, –3.2; IR (thin film) 1428, 1102 cm^{–1}; HRMS (ESI) *m/z* calcd for C₁₆H₂₆NaOSi (M + Na)⁺ 285.1651 found 285.1655. Anal. Calcd for C₁₆H₂₆OSi: C, 73.22; H, 9.98. Found: C, 73.29; H, 10.11.

II. Synthesis of Enantioenriched α-Silyloxy Allylic Silane (–)-14 by Asymmetric Reduction

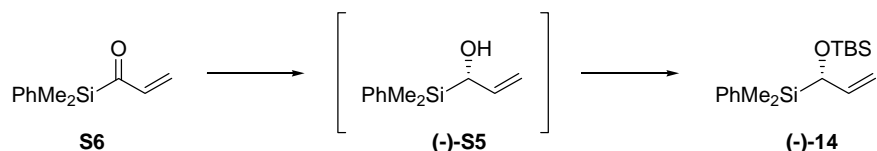


Allylic Silylether S4. To a cooled (–78 °C) solution of allylic alcohol (1.00 mL, 14.7 mmol), PhMe₂SiCl (3.70 mL, 22.1 mmol), and DMAP (0.900 g, 7.35 mmol) in CH₂Cl₂ (50 mL) was added triethylamine (3.83 mL, 29.4 mmol). The reaction mixture was stirred at 24 °C for 36 h. The reaction mixture was diluted H₂O (15 mL) and the CH₂Cl₂ was removed *in vacuo*. The resulting slurry was diluted with saturated aqueous NH₄Cl (20 mL) and hexanes (20 mL). The layers were separated, and the aqueous layer was extracted with hexanes (3 × 15 mL). The combined organic layers were washed with saturated aqueous NaCl (25 mL). The resultant organic phase was dried with Na₂SO₄ and filtered. The filtrate was concentrated *in vacuo* to afford unpurified **S4** as a pink oil. Purification by flash chromatography (hexanes to 15:85 EtOAc/hexanes) provided **S4** as a colorless oil (2.44 g, 86%). Spectral data were identical to those reported in literature:⁷ ¹H NMR (CDCl₃, 400 MHz) δ 7.59 (m, 2H), 7.38 (m, 3H), 5.96–5.86 (ddt, *J* = 17.1, 10.3, 4.9, 1H), 5.26 (ddd, *J* = 17.1, 3.6, 1.8, 1H), 5.09 (ddd, *J* = 10.4, 3.3, 1.6, 1H), 4.15 (ddd, *J* = 4.9, 1.6, 1.6, 2H), 0.40 (s, 6H); ¹³C NMR (CDCl₃, 125 MHz) δ 137.9, 137.2, 133.7, 129.9, 128.1, 114.9, 64.3, –1.48; IR (thin film) 3070, 2960, 1428, 1252 cm^{–1}.



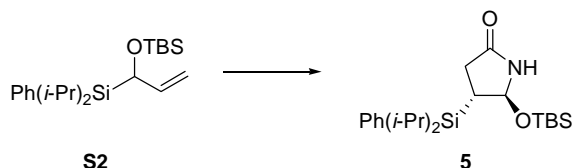
Acyl Silane S6. To a cooled (–78 °C) solution of **S4** (8.00 g, 41.6 mmol), and LiCl (5.30 g, 125 mmol) in THF (200 mL) was added *s*-BuLi (93.8 mL, 1.30 M in 92:8 cyclohexane/hexanes, 125 mmol). The reaction mixture was stirred at –78 °C for 45 min. The reaction mixture was poured onto a vigorously stirring saturated solution of aqueous NH₄Cl (1200 mL). The layers were separated, and the aqueous layer was extracted with EtOAc (3 × 200 mL). The combined organic layers were washed with saturated aqueous NaCl (150 mL). The resultant organic phase was dried with Na₂SO₄ and filtered. The filtrate was concentrated *in vacuo* to afford α-hydroxy allylic silane **S5** as a yellow oil. Spectral data were identical to those reported in literature:⁸ ¹H NMR (CDCl₃, 500 MHz) δ 7.57 (m, 2H), 7.38 (m, 3H), 6.00 (ddd, *J* = 17.1, 10.7, 5.3, 1H), 5.06 (ddd, *J* = 17.2, 1.7, 1.7, 1H), 5.00 (ddd, *J* = 10.7, 1.7, 1.7, 1H), 4.22 (ddd, *J* = 5.3, 2.0, 2.0, 1H), 0.35 (s, 3H), 0.33 (s, 3H); ¹³C NMR (CDCl₃, 125 MHz) δ 139.5, 136.2, 134.3, 129.6, 128.0, 110.2, 68.6, –5.6, –5.9; HRMS (ESI) *m/z* calcd for C₁₁H₁₆NaOSi (M + Na)⁺ 215.0868, found 215.0870.

In a separate flask, to a solution of trifluoroacetic anhydride (8.70 mL, 62.4 mmol) in CH₂Cl₂ (80 mL) was cooled to –78 °C as a solution of DMSO (5.90 mL, 83.2 mmol) in CH₂Cl₂ (60 mL) was added dropwise. After stirring for 30 minutes at –78 °C, a solution of α-hydroxy allylic silane **S5** in CH₂Cl₂ (80 mL) was added over 30 min. After stirring for 1 h at –78 °C, triethylamine (17.4 mL, 125 mmol) was added dropwise. The solution was stirred at –78 °C for 1 h. The reaction mixture was diluted with H₂O (150 mL) and warmed to 24 °C. The layers were separated and the aqueous layer was extracted with CH₂Cl₂ (3 × 50 mL). The combined organic layers were washed with saturated aqueous NaCl (200 mL). The resultant organic phase was dried over MgSO₄ and filtered. The filtrate was concentrated *in vacuo* to afford unpurified **S6** as a yellow oil. Purification by flash chromatography (5:95 to 10:90 EtOAc/hexanes) provided **S6** as a vibrant yellow oil (7.00 g, 89%). Spectral data were identical to those reported in literature:⁸ ¹H NMR (CDCl₃, 500 MHz) δ 7.55 (m, 2H), 7.40 (m, 3H), 6.41 (dd, *J* = 17.9, 10.8, 1H), 5.98 (d, *J* = 17.9, 1H), 5.87 (d, *J* = 10.8, 1H), 0.53 (s, 6H); ¹³C NMR (CDCl₃, 125 MHz) δ 236.0, 141.3, 135.3, 134.1, 130.0, 129.7, 128.4, –3.6; IR (thin film) 2962, 1638, 1598, 1430, 1250 cm^{–1}; HRMS (ESI) *m/z* calcd for C₁₁H₁₄NaOSi (M + Na)⁺ 213.0712, found 213.0708.



Allylic Silane (–)-14. To a cooled ($-78\text{ }^\circ\text{C}$) solution of (+)-diisopinocampheylchloroborane (11.33 g, 35.31 mmol) in THF (30 mL) was added a solution of **S6** (5.60 g, 29.4 mmol) in THF (30 mL). The reaction mixture was warmed to $24\text{ }^\circ\text{C}$ and stirred for 60 h. Acetaldehyde (3.30 mL, 58.8 mmol) was added, and the reaction was stirred at $24\text{ }^\circ\text{C}$ for 2.5 h. The reaction mixture was concentrated *in vacuo*, and the residual pinene was removed under reduced pressure (~ 0.1 Torr). The resulting slurry was dissolved in Et_2O (200 mL) and diethanolamine (11.3 mL, 118 mmol) was added. The reaction mixture was stirred at $24\text{ }^\circ\text{C}$ for 20 h. The resulting suspension was filtered through Celite[®], and the solids were washed with Et_2O . The filtrate was concentrated *in vacuo* to afford α -hydroxy allylic silane (–)-**S5** as a clear oil. α -Hydroxy allylic silane (–)-**S5** was isolated in 93% *ee* by chiral HPLC (Chiralcel OD-H column, 99.5:0.5 hexanes/IPA, 1 mL/min, 220/254 nm), $[\alpha]_D^{23} -10.5$ (*c* 0.50, CHCl_3). Spectral data for (–)-**S5** were identical to those reported in literature.⁸ α -Hydroxy allylic silane (–)-**S5** was dissolved in DMF (60 mL) and stirred at $24\text{ }^\circ\text{C}$ as TBDMSCl (8.87 g, 58.8 mmol) and imidazole (3.00 g, 44.1 mmol) were added. The reaction mixture was stirred at $24\text{ }^\circ\text{C}$ for 18 h. The reaction mixture was diluted with saturated aqueous NH_4Cl (100 mL) and hexanes (50 mL). The layers were separated and aqueous layer was extracted with hexanes (3×30 mL). The combined organic layers were washed with saturated aqueous NaCl (50 mL). The resultant organic phase was dried with MgSO_4 and filtered. The filtrate was concentrated *in vacuo* to afford unpurified (–)-**14** as a colorless oil. Purification by flash chromatography (hexanes) provided (–)-**14** as a colorless oil (8.34 g, 93%). Spectral data were identical to those reported in literature:⁹ ^1H NMR (CDCl_3 , 400 MHz) δ 7.53 (m, 2H), 7.34 (m, 3H), 5.83 (ddd, $J = 17.1, 10.6, 5.3$, 1H), 5.02 (d, $J = 17.0$, 1H), 4.89 ($J = 10.6$, 1H), 4.12 (d, $J = 5.2$, 1H), 0.87 (s, 9H), 0.31 (s, 3H), 0.27 (s, 3H), -0.06 (s, 3H), -0.15 (s, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 139.4, 137.2, 134.5, 129.3, 127.7, 110.4, 68.9, 26.0, 18.4, -4.4 , -5.2 , -5.7 , -5.8 ; IR (thin film) 2958, 2858, 1252 cm^{-1} ; Anal. Calcd for $\text{C}_{17}\text{H}_{30}\text{OSi}_2$: C, 66.60; H, 9.86. Found: C, 66.70; H, 10.01. $[\alpha]_D^{23} -7.0$ (*c* 0.35, CHCl_3).

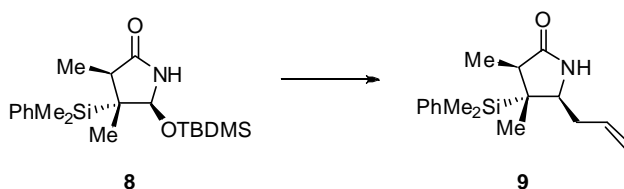
III. [3+2] Cycloaddition of α -Silyloxy Allylic Silanes and Chlorosulfonyl Isocyanate



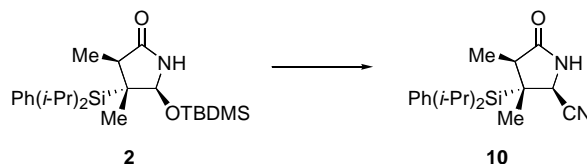
γ -Lactam 5. To a cooled ($0\text{ }^\circ\text{C}$) solution of α -silyloxy allylic silane **S2** (0.750 g, 2.07 mmol) in CH_2Cl_2 (15 mL) was added chlorosulfonyl isocyanate (0.27 mL, 3.1 mmol). The reaction mixture was stirred at $0\text{ }^\circ\text{C}$ for 1 h. The reaction mixture was diluted with saturated aqueous NaHCO_3 (5 mL), and the CH_2Cl_2 removed *in vacuo*. The resultant aqueous layer was diluted with saturated aqueous NH_4Cl (10 mL) and EtOAc (10 mL). The layers were separated, and the aqueous layer was extracted with EtOAc (3×5 mL). The combined organic layers were washed with saturated aqueous NaCl (15 mL). The resultant organic phase was dried over Na_2SO_4 and filtered. The filtrate was concentrated *in vacuo* to afford the *N*-chlorosulfonyl γ -lactam as a clear oil. The *N*-chlorosulfonyl γ -lactam was dissolved in toluene (30 mL) and cooled to $-78\text{ }^\circ\text{C}$ Red-Al[®] (0.95 mL, 65 % w/w solution in toluene, 3.1 mmol) was added dropwise. After 1 h, the reaction mixture was diluted with water (0.62 mL), and stirred at $24\text{ }^\circ\text{C}$ for 1 h. The resultant slurry was filtered, and the solids washed with toluene (10 mL). The filtrate was concentrated *in vacuo*, to afford unpurified **5** as a white slurry. Purification by flash chromatography (30:70 EtOAc /hexanes) provided **5** as a white solid (0.465 g, 55%, $>95:5$ diastereomer ratio as determined by ^1H NMR spectroscopy): mp $131\text{--}134\text{ }^\circ\text{C}$; ^1H NMR (CDCl_3 , 400 MHz) δ 7.48 (m, 2H), 7.38 (3H), 6.01 (br s, 1H), 5.35 (s, 1H), 2.82 (dd, $J = 17.6, 11.0$, 1H), 2.26 (dd, $J = 17.6, 4.6$, 1H), 2.16 (ddd, $J = 11.0, 4.6, 2.0$, 1H), 1.34–1.45 (m, 2H), 1.08 (m, 12H), 0.88 (s, 9H), 0.04 (s, 3H), 0.01 (s, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 178.5, 135.1, 132.9, 129.5, 128.1, 82.0, 31.0, 28.5, 25.8, 18.4, 18.3, 17.8, 10.9, 10.8, -4.0 , -4.6 ; IR (thin film) 3199, 1702 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{22}\text{H}_{39}\text{NNaO}_2\text{Si}_2$ ($M + \text{Na}$)⁺ 428.2417, found 428.2404. Anal. Calcd for $\text{C}_{22}\text{H}_{39}\text{NO}_2\text{Si}_2$: C, 65.13; H, 9.69. Found: C, 65.19; H, 9.81.

Lactam 7. To a cooled (−78 °C) solution of lactam **2** (0.100 g, 0.231 mmol) in THF (2 mL) was added allylmagnesium chloride (0.35 mL, 0.69 mmol). The reaction mixture was warmed to 24 °C over 2 h. After stirring for 3 h at 24 °C, the reaction mixture was cooled to 0 °C, and saturated aqueous NH₄Cl (10 mL) was added dropwise. The layers were separated, and the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with saturated aqueous NaCl (15 mL). The resultant organic phase was dried with MgSO₄ and filtered. The filtrate was concentrated *in vacuo* to afford unpurified **7** as a colorless oil. Purification by flash chromatography (20:80 to 40:60 EtOAc/hexanes) provided **7** as a white solid (0.065 g, 82%, >95:5 diastereomer ratio as determined by ¹H NMR spectroscopy): mp 131–134 °C; ¹H NMR (CDCl₃, 400 MHz) δ 7.51 (m, 2H), 7.37 (m, 3H), 5.68–5.55 (dddd, *J* = 16.9, 10.2, 9.0, 5.1, 1H), 5.49 (br s, 1H), 5.05 (dd, *J* = 10.0, 1.0, 1H), 5.01 (dd, *J* = 16.9, 1.0, 1H), 3.77 (dd, *J* = 11.0, 2.2, 1H), 2.79 (q, *J* = 7.3, 1H), 1.96 (ddd, *J* = 13.8, 5.0, 1.9, 1H), 1.84 (ddd, *J* = 13.8, 11.0, 9.0, 1H), 1.68–1.56 (m, 2H), 1.33 (d, *J* = 7.4, 6H), 1.19 (d, *J* = 7.5, 3H), 1.17 (d, *J* = 7.5, 3H), 1.03 (s, 3H), 1.02 (d, *J* = 7.3, 3H); ¹³C NMR (CDCl₃, 125 MHz) δ 179.2, 135.8, 135.6, 134.6, 129.2, 127.9, 118.0, 57.0, 43.4, 36.6, 32.9, 20.6, 20.5, 19.8, 19.7, 13.7, 11.8, 11.7, 11.6; IR (thin film) 3199, 1696 cm^{−1}; HRMS

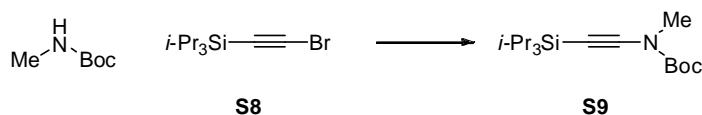
(ESI) m/z calcd for $C_{21}H_{34}NOSi$ ($M + H$)⁺ 344.2410, found 344.2407. Anal. Calcd for $C_{21}H_{33}NOSi$: C, 73.41; H, 9.68. Found: C, 73.16; H, 9.69.



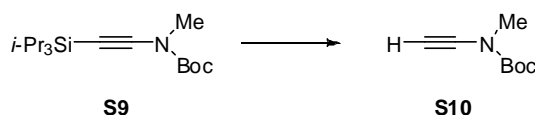
Lactam 9. To a cooled (−78 °C) solution of lactam **8**⁹ (1.00 g, 2.65 mmol) in toluene (150 mL) was added allylmagnesium chloride (2.92 mL, 5.83 mmol). The reaction mixture was warmed to 24 °C over 12 h. The reaction mixture was cooled to 0 °C and saturated aqueous NH_4Cl (75 mL) was added. The layers were separated, and the aqueous layer was extracted with EtOAc (3 × 30 mL). The combined organic layers were washed with saturated aqueous NaCl (100 mL). The resultant organic phase was dried with $MgSO_4$ and filtered. The filtrate was concentrated *in vacuo* to afford unpurified **9** as an 85:15 mixture of diastereomers. Purification by flash chromatography (50:50 EtOAc/hexanes to EtOAc) provided **9** as a clear oil (0.635 g, 83%, 85:15 diastereomer ratio as determined by 1H NMR spectroscopy): 1H NMR ($CDCl_3$, 500 MHz) δ 7.50 (m, 2H), 7.40 (m, 3H), 5.65 (m, 1H), 5.46 (br s, 1H), 5.04 (m, 2H), 3.57 (dd, J = 10.5, 2.7, 1H), 2.57 (q, J = 7.3, 1H), 1.85 (m, 2H), 1.00 (d, J = 7.3, 3H), 0.94 (s, 3H), 0.41 (s, 3H), 0.40 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 179.0, 136.3, 135.5, 134.4, 129.8, 128.2, 118.0, 56.5, 43.4, 36.0, 32.3, 11.3, 10.6, −4.5, −4.7; IR (thin film) 3205, 1698, 1428, 1252 cm^{-1} ; HRMS (ESI) m/z calcd for $C_{17}H_{25}NNaOSi$ ($M + Na$)⁺ 310.1603, found 310.1601.



Nitrile 10. To a solution of **2** (2.00 g, 4.61 mmol) in toluene (10 mL) was added Et_2AlCN (23.0 mL, 1.0 M in toluene, 23 mmol). The reaction mixture was heated at 50 °C for 24 h. The reaction mixture was cooled to 0 °C and a 1 N solution of aqueous HCl (20 mL) was added. The layers were separated and the aqueous layer was extracted with EtOAc (3 × 15 mL). The combined organic layers were washed with saturated aqueous NaCl (25 mL). The resultant organic phase was dried with $MgSO_4$ and filtered. The filtrate was concentrated *in vacuo* to afford unpurified **10** as a viscous oil. Purification by flash chromatography (30:70 to 50:50 EtOAc/hexanes) provided **10** as a white foam (1.26 g, 84%, >95:5 diastereomer ratio as determined by 1H NMR spectroscopy): 1H NMR ($CDCl_3$, 400 MHz) δ 7.49 (m, 2H), 7.39 (m, 3H), 7.21 (br s, 1H), 4.56 (s, 1H), 2.61 (q, J = 7.4, 1H), 1.64 (m, 2H), 1.37 (s, 3H), 1.34 (d, J = 7.4, 3H), 1.32 (d, J = 7.4, 3H), 1.21 (d, J = 7.5, 3H), 1.16 (d, J = 7.6, 3H), 1.05 (d, J = 7.4, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 180.2, 135.6, 132.7, 130.0, 128.5, 117.4, 50.8, 42.0, 32.5, 20.4, 19.6, 19.5, 16.8, 11.7, 11.5, 11.4; IR (thin film) 3207, 1706 cm^{-1} ; HRMS (ESI) m/z calcd for $C_{19}H_{29}N_2OSi$ ($M + H$)⁺ 329.2049, found 329.2044.



Alkynylamide S9. A suspension of *tert*-butyl-*N*-methylcarbamate¹⁰ (4.00 g, 15.2 mmol), **S8**¹¹ (2.00 g, 15.3 mmol), $CuSO_4 \cdot 5H_2O$ (0.373 g, 1.53 mmol), K_3PO_4 (6.47 g, 30.5 mmol) and 1,10-phenanthroline (0.550 g, 3.05 mmol) in toluene (15 mL) was stirred at 80 °C for 60 h. The reaction mixture was filtered through Celite® and the solids were washed the hexanes. The filtrate was concentrated *in vacuo* to afford unpurified **S9** as a brown oil. Purification by flash chromatography (5:95 to 15:85 EtOAc/hexanes) provided **S9** as a colorless oil (3.10 g, 65%): 1H NMR ($CDCl_3$, 400 MHz) δ 3.11 (s, 3H), 1.48 (s, 9H), 1.07 (s, 21H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 154.7, 99.3, 66.5, 37.4, 28.3, 18.8, 11.6; IR (thin film) 2943, 2865, 1725, 1465 cm^{-1} ; HRMS (ESI) m/z calcd for $C_{17}H_{33}NNaO_2Si$ ($M + Na$)⁺ 334.2178, found 334.2177. Anal. Calcd for $C_{17}H_{33}NO_2Si$: C, 65.54; H, 10.68. Found: C, 65.64; H, 10.72.



Alkynylamide S10. To a cooled (0 °C) solution of **S9** (3.00 g, 9.63 mmol) in THF (70 mL) was added *t*-Bu₄NF (10.60 mL, 1.0 M in THF, 11 mmol). The reaction mixture was stirred at 24 °C for 45 min. The reaction mixture was poured into H₂O (50 mL) and the layers were separated. The aqueous layer was extracted with pentane (3 × 30 mL). The combined organic layers were washed with

C#CN(C)C(=O)OC(C)(C)C (S10) + CC1(C)NC(=O)C(C1)OSi(C)(C)C2=CC=CC=C2C3=CC=CC=C3 (8) → CC1(C)NC(=O)C(C1)C#CC(C)N(C)C(=O)OC(C)(C)C (11)

Chemical reaction scheme showing the synthesis of compound **12** from S11 and **2**.

Reactants:

- S11: $\text{CH}_3\text{C}\equiv\text{CCN}(\text{Bu})_2$
- 2**: A substituted pyrrolidin-2-one with a methyl group, a PhMe_2SiMe group, and an OTBDMS group.

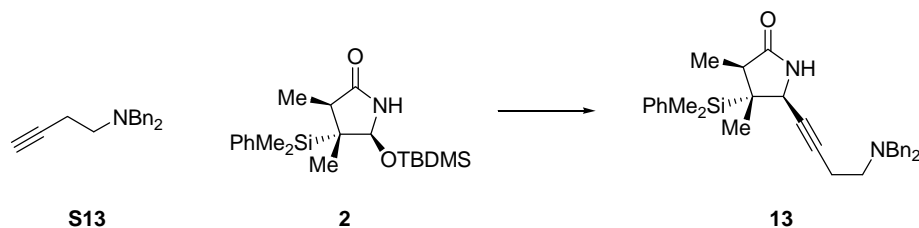
Product:

- 12**: A substituted pyrrolidin-2-one where the OTBDMS group has been replaced by the $\text{CH}_3\text{C}\equiv\text{CCN}(\text{Bu})_2$ group.

S12 **S13**

Alkyne S13. To a suspension of **S12**¹³ (7.30 g, 32.5 mmol) and K₂CO₃ (6.75 g, 48.8 mmol) in DMF (15 mL) was added dibenzylamine (9.40 mL, 48.8 mmol). The resulting suspension was heated at 50 °C for 36 h. The reaction mixture was cooled to 24 °C and diluted with saturated aqueous ammonium chloride (50 mL). The resulting heterogeneous mixture was extracted with EtOAc (3 × 30 mL). The combined organic layers were washed with saturated aqueous NaCl (40 mL). The resultant organic phase was dried with MgSO₄ and filtered. The filtrate was concentrated *in vacuo* to afford unpurified **S13** as a yellow oil. Purification by flash

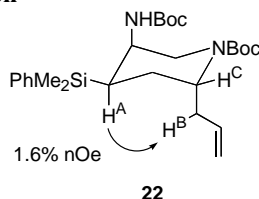
chromatography (10:90 EtOAc/hexanes) provided **S13** as a colorless oil (5.63 g, 69%): ^1H NMR (CDCl_3 , 400 MHz) δ 7.38 (m, 4H), 7.30 (m, 4H), 7.23 (m, 2H), 3.62 (s, 4H), 2.70 (t, $J = 7.2$, 2H), 2.35 (dt, $J = 7.2$, 2.6, 2H), 1.93 (t, $J = 2.6$, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 139.6, 128.8, 128.4, 127.1, 83.2, 69.2, 58.2, 52.2, 17.2; IR (thin film) 3299 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{18}\text{H}_{20}\text{N}$ ($\text{M} + \text{H}$) $^+$ 250.1596, found 250.1592. Anal. Calcd for $\text{C}_{18}\text{H}_{19}\text{N}$: C, 86.70; H, 7.68. Found: C, 86.48; H, 7.68.



γ -Lactam 13. To a cooled ($-42\text{ }^\circ\text{C}$) solution of **S13** (0.576 g, 2.31 mmol) in toluene (4 mL) was added $n\text{-BuLi}$ (0.93 mL, 2.60 M in hexanes, 2.42 mmol). After 15 min, Me_2AlCl (2.31 mL 1.0 M in hexanes, 2.3 mmol) was added, and the reaction mixture was warmed to $0\text{ }^\circ\text{C}$. After 15 min, a solution of **2** (0.200 g, 0.460 mmol) in toluene (6 mL) was added, and the resulting solution was heated to $50\text{ }^\circ\text{C}$ for 5 h. The reaction mixture was cooled to $24\text{ }^\circ\text{C}$ and diluted with saturated aqueous sodium potassium tartrate (20 mL). The layers were separated, and the aqueous layer was extracted with EtOAc ($3 \times 15\text{ mL}$). The combined organic layers were washed with saturated aqueous NaCl (20 mL). The resultant organic phase was dried with MgSO_4 and filtered. The filtrate was concentrated *in vacuo* to afford unpurified **13** as a yellow oil. Purification by flash chromatography (20:80 to 40:60 EtOAc/hexanes) provided **13** as a white solid (0.229 g, 90%, >95:5 diastereomer ratio as determined by ^1H NMR spectroscopy): mp $147\text{--}149\text{ }^\circ\text{C}$; ^1H NMR (CDCl_3 , 400 MHz) δ 7.48 (m, 2H), 7.40–7.30 (m, 11H), 7.25 (m, 2H), 5.21 (br s, 1H), 4.45 (s, 1H), 3.61 (s, 4H), 2.64 (t, $J = 7.3$, 2H), 2.49 (q, $J = 7.2$, 1H), 2.35 (dt, $J = 7.3$, 1.8, 2H), 1.71–1.58 (m, 2H), 1.32 (d, $J = 6.4$, 3H), 1.30 (d, $J = 7.2$, 3H), 1.19 (s, 3H), 1.16 (d, $J = 7.6$, 3H), 1.12 (d, $J = 7.5$, 3H), 0.95 (d, $J = 7.3$, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 178.9, 139.5, 135.8, 134.2, 129.2, 128.8, 128.4, 128.0, 127.1, 85.8, 77.7, 58.3, 52.2, 50.7, 42.7, 34.9, 20.6, 19.8, 19.7, 17.5, 15.4, 11.9, 11.8, 11.2; IR (thin film) 3205 , 1698 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{36}\text{H}_{47}\text{N}_2\text{OSi}$ ($\text{M} + \text{H}$) $^+$ 551.3458, found 551.3445. Anal. Calcd for $\text{C}_{36}\text{H}_{46}\text{N}_2\text{OSi}$: C, 78.49; H, 8.42. Found: C, 78.24; H, 8.42.

V. Stereochemistry and Structural Proofs

A. Stereoselectivity of N,O -acetal substitution



Piperidine **22**.

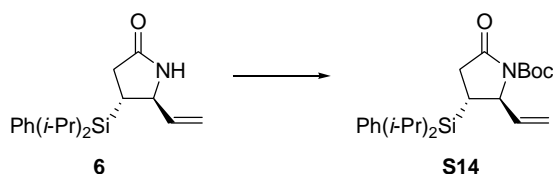
nOe experiment was performed for **22** using a pure sample.

H^{A} irradiated: H^{B} (1.6%), H^{C} (0%)

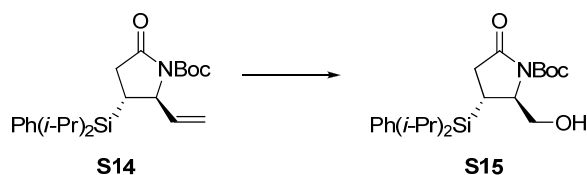
Note: The observation on nOe between H^{A} and H^{B} and the absence of nOe between H^{A} and H^{C} suggests a 1,3 trans conformation.

B. Proof of Translactamization versus Acyl-transfer

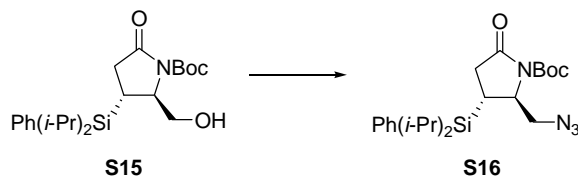
δ -Lactam **S17** was formed by reduction and translactamization of azide **S16**. γ -Lactam **S19** was formed by the reduction of γ -lactam **S18** (translactamization does not occur when the lactam nitrogen is not activated). The amine of lactam **S19** was protected as the toluenesulfonate amide (**S21**), and its structure confirmed by X-ray crystallography (See Section XII for crystallographic data). The amine of lactam **S19** was protected as the *tert*-butyl carbamate (**S22**), which would be the product of acyl-transfer upon reduction of azide **S16**. The spectral data of the isolated δ -lactam (**S17**) and γ -lactam **S22** do not match, thus confirming translactamization as the major reaction pathway.



Alkene S14. To a solution of **6** (0.215 g, 0.713 mmol) and DMAP (0.105 g, 0.856 mmol) in MeCN (20 mL) at 24 °C was added di-*tert*-butyl dicarbonate (0.33 mL, 1.4 mmol). The reaction mixture was stirred at 24 °C for 3 h. The reaction mixture was diluted with saturated aqueous NH₄Cl (30 mL). The layers were separated, and the aqueous layer was extracted with EtOAc (3 × 15 mL). The combined organic layers were washed with saturated aqueous NaCl (40 mL). The resultant organic phase was dried with Na₂SO₄ and filtered. The filtrate was concentrated *in vacuo* to afford unpurified **S14** as a yellow oil. Purification by flash chromatography (10:90 to 50:50 EtOAc/hexanes) provided **S14** as a white solid (0.268 g, 94%, >95:5 diastereomer ratio as determined by ¹H NMR spectroscopy): mp 80–82 °C; ¹H NMR (CDCl₃, 400 MHz) δ 7.46 (m, 2H), 7.38 (m, 3H), 5.86 (ddd, *J* = 16.8, 10.3, 7.0, 1H), 5.14 (d, *J* = 10.3, 1H), 5.11 (d, *J* = 16.8, 1H), 4.56 (dd, *J* = 7.0, 3.0, 1H), 2.87 (dd, *J* = 18.1, 11.3, 1H), 2.46 (dd, *J* = 18.1, 4.0, 1H), 1.80 (ddd, *J* = 11.2, 3.9, 3.1, 1H), 1.52–1.42 (m, 2H), 1.43 (s, 9H), 1.09 (m, 12H); ¹³C NMR (CDCl₃, 125 MHz) δ 174.3, 149.6, 138.1, 135.0, 132.3, 129.7, 128.2, 115.3, 82.8, 61.4, 33.5, 28.0, 19.8, 18.4, 18.3, 18.2, 18.1, 10.6, 10.5; IR (thin film) 1785, 1750, 1719 cm⁻¹; HRMS (ESI) *m/z* calcd for C₂₃H₃₅NNaO₃Si (M + Na)⁺ 424.2284, found 424.2293. Anal. Calcd for C₂₃H₃₅NO₃Si: C, 68.78; H, 8.78. Found: C, 68.88; H, 8.83.

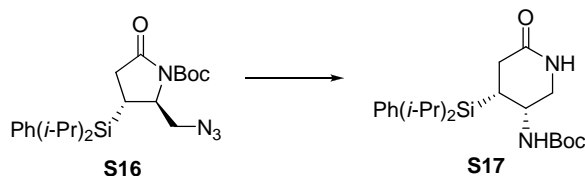


Alcohol S15. To a cooled (–78 °C) solution of **S14** (0.300 g, 0.747 mmol) in MeOH (8 mL) was bubbled ozone. When the solution became bright blue, oxygen was bubbled through the solution until it became clear. Sodium borohydride (0.085 g, 2.2 mmol) was added, and the reaction mixture warmed to 0 °C. The reaction mixture was stirred at 0 °C for 30 minutes. The reaction mixture was diluted with H₂O (10 mL) and EtOAc (10 mL). The layers were separated, and the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with saturated aqueous NaCl (20 mL). The resultant organic phase was dried with MgSO₄ and filtered. The filtrate was concentrated *in vacuo* to afford unpurified **S15** as a white solid. Purification by flash chromatography (30:70 to 70:30 EtOAc/hexanes) provided **S15** as a white solid (0.300 g, 99%, >95:5 diastereomer ratio as determined by ¹H NMR spectroscopy): mp 128–131 °C; ¹H NMR (CDCl₃, 400 MHz) δ 7.46 (m, 2H), 7.36 (m, 3H), 4.21 (m, 1H), 3.91 (ddd, *J* = 11.6, 5.5, 3.4, 1H), 3.65 (ddd, *J* = 11.6, 6.7, 3.9, 1H), 3.03 (dd, *J* = 18.3, 11.8, 1H), 2.80 (dd, *J* = 3.9, 3.4, 1H), 2.41 (dd, *J* = 18.3, 3.3, 1H), 2.04 (m, 1H), 1.48–1.40 (m, 2H), 1.46 (s, 9H), 1.08 (m, 12H); ¹³C NMR (CDCl₃, 125 MHz) δ 175.4, 150.2, 134.9, 132.5, 129.6, 128.2, 83.1, 65.7, 61.3, 34.7, 28.1, 18.4, 18.3, 18.2, 18.1, 15.6, 10.5, 10.4; IR (thin film) 3450, 1775, 1719 cm⁻¹; HRMS (ESI) *m/z* calcd for C₂₂H₃₅NNaO₄Si (M + Na)⁺ 428.2233, found 428.2229. Anal. Calcd for C₂₂H₃₅NO₄Si: C, 65.15; H, 8.70. Found: C, 65.14; H, 8.73.

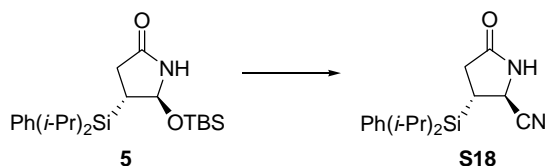


Azide S16. To a solution of **S15** (1.46 g, 3.60 mmol), toluenesulfonyl chloride (0.824 g, 4.32 mmol), and DMAP (0.484 g, 3.96 mmol) in CH₂Cl₂ (20 mL) at 24 °C was added Et₃N (1.00 mL, 7.20 mmol). The reaction mixture was stirred at 24 °C for 12 h. The reaction mixture was concentrated *in vacuo*, and diluted with saturated aqueous NH₄Cl (20 mL) and EtOAc (20 mL). The layers were separated, and the aqueous layer was extracted with EtOAc (3 × 15 mL). The combined organic layers were washed with saturated aqueous NaCl (30 mL). The resultant organic phase was dried with MgSO₄ and filtered. The filtrate was concentrated *in vacuo* to afford unpurified **S16** as a yellow oil. Purification by flash chromatography (15:85 to 50:50 EtOAc/hexanes) provided **S16** as a white solid (1.31 g, 85%, >95:5 diastereomer ratio as determined by ¹H NMR spectroscopy): mp 82–84 °C; ¹H NMR (CDCl₃, 500 MHz) δ 7.46 (m, 2H), 7.38 (m, 3H), 4.24 (m, 1H), 3.66 (dd, *J* = 12.3, 5.4, 1H), 3.46 (dd, *J* = 12.3, 2.8, 1H), 2.99 (dd, *J* = 18.3, 11.7, 1H), 2.45 (dd, *J* = 18.3, 3.1, 1H), 1.93 (m, 1H), 1.51–1.40 (m, 2H), 1.47 (s, 9H), 1.11 (s, 6H), 1.09 (s, 6H); ¹³C NMR (CDCl₃, 125 MHz) δ 173.7, 149.8, 134.8,

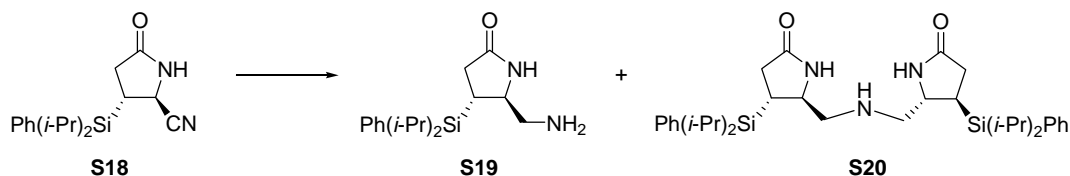
132.1, 129.8, 128.3, 83.5, 58.3, 54.9, 33.9, 28.1, 18.4, 18.3, 18.2, 18.1, 16.6, 10.5, 10.3; IR (thin film) 2113, 1789, 1752, 1713 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{22}\text{H}_{34}\text{N}_4\text{NaO}_3\text{Si}$ ($\text{M} + \text{Na}$)⁺ 453.2298, found 453.2303. Anal. Calcd for $\text{C}_{22}\text{H}_{34}\text{N}_4\text{O}_3\text{Si}$: C, 61.36; H, 7.96. Found: C, 61.69; H, 7.79.



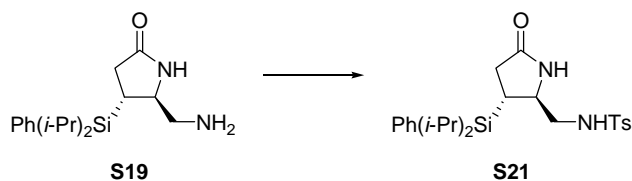
δ -Lactam S17. A suspension of **S16** (0.475 g, 1.17 mmol) and 10% Pd/C (0.117 g) in MeOH (23 mL) at 24°C was stirred under an atmosphere of H_2 for 18 hr. The reaction mixture was filtered through Celite® and concentrated *in vacuo* to afford a colorless oil. The oil was dissolved in toluene (60 mL) and acetic acid (0.03 mL, 0.6 mmol) was added. The reaction mixture was heated at reflux for 24 h. The reaction mixture was concentrated *in vacuo* to afford unpurified **S17** as an orange oil. Purification by flash chromatography (EtOAc) provided **S17** as a white foam (0.346 g, 73%, >95:5 diastereomer ratio as determined by ^1H NMR spectroscopy): ^1H NMR (CDCl_3 , 400 MHz) δ 7.49 (m, 2H), 7.38 (m, 3H), 5.92 (br s, 1H), 4.75 (br s, 1H), 3.80 (m, 1H), 3.22–3.05 (m, 2H), 2.60 (dd, $J = 17.5$, 11.1, 1H), 2.36 (dd, $J = 17.5$, 7.5, 1H), 1.90 (m, 1H), 1.51–1.38 (m, 2H), 1.44 (s, 9H), 1.11 (m, 12H). HRMS (ESI) m/z calcd for $\text{C}_{22}\text{H}_{37}\text{N}_2\text{O}_3\text{Si}$ ($\text{M} + \text{H}$)⁺ 405.2574, found 405.2577.



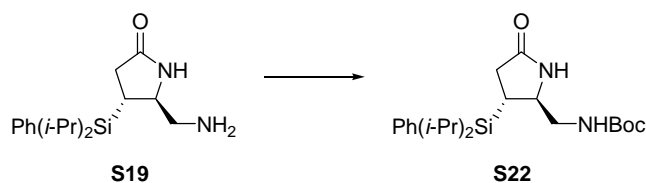
Nitrile S18. To a cooled (-78°C) solution of **5** (1.10 g, 2.71 mmol) and Me_3SiCN (1.10 mL, 8.13 mmol) in CH_2Cl_2 (35 mL) was added $\text{BF}_3 \cdot \text{OEt}_2$ (0.68 mL, 5.4 mmol). The reaction was warmed to 24°C over 6 h. The reaction mixture was diluted with saturated aqueous NaHCO_3 (15 mL), and the CH_2Cl_2 removed *in vacuo*. The resultant aqueous layer was diluted with saturated aqueous NH_4Cl (10 mL) and EtOAc (20 mL). The layers were separated, and the aqueous layer was extracted with EtOAc (3×15 mL). The combined organic layers were washed with saturated aqueous NaCl (35 mL). The resultant organic phase was dried over Na_2SO_4 and filtered. The filtrate was concentrated *in vacuo* to afford unpurified **S18** as a brown oil. Purification by flash chromatography (20:80 to 30:70 EtOAc/hexanes) provided **S18** as a white solid (0.681 g, 84%, >95:5 diastereomer ratio as determined by ^1H NMR spectroscopy): ^1H NMR (CDCl_3 , 400 MHz) δ 7.47 (m, 2H), 7.42 (m, 3H), 6.40 (br s, 1H), 4.29 (d, $J = 6.8$, 1H), 2.70 (dd, $J = 17.0$, 10.6, 1H), 2.51 (ddd, $J = 10.6$, 7.8, 6.5, 1H), 2.34 (dd, $J = 17.0$, 7.8, 1H), 1.54–1.43 (m, 2H), 1.19 (d, $J = 7.5$, 3H), 1.16 (d, $J = 7.5$, 3H), 1.15 (d, $J = 7.4$, 3H), 1.14 (d, $J = 7.4$, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 177.5, 135.0, 131.2, 130.3, 128.7, 119.3, 45.2, 31.3, 23.4, 18.7, 18.6, 18.5, 18.4, 11.1, 11.0; IR (thin film) 3218, 1702 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{17}\text{H}_{24}\text{N}_2\text{ONaSi}$ ($\text{M} + \text{Na}$)⁺ 323.1555, found 323.1557.



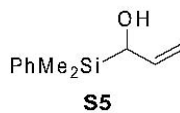
Amine S19 and Bis-lactam S20. To a suspension of **S18** (0.100 g, 0.333 mmol) and Pd/C (100 mg) in MeOH (7 mL) was stirred at 24°C for 6 h. The reaction mixture was filtered through Celite® and concentrated *in vacuo* to provide the unpurified mixture of **S19** and **S20** as a colorless oil. Purification by flash chromatography (EtOAc to 50:50 MeOH/EtOAc) provided **S19** as a white foam (0.040 g, 40%) and **S20** as a white foam (0.030 g, 30%). Spectral data for **S19**: ^1H NMR (CDCl_3 , 400 MHz) δ 7.48 (m, 2H), 7.38 (m, 3H), 6.28 (br s, 1H), 3.71 (m, 1H), 2.86 (dd, $J = 12.8$, 3.2, 1H), 2.61 (dd, $J = 17.4$, 11.0, 1H), 2.55 (dd, $J = 12.8$, 7.9, 1H), 2.38 (dd, $J = 17.5$, 7.8, 1H), 1.86 (ddd, $J = 11.1$, 7.7, 6.0, 1H), 1.85–1.70 (br s, 2H), 1.51–1.34 (m, 2H), 1.12 (d, $J = 7.5$, 3H), 1.11 (d, $J = 7.5$, 3H), 1.10 (d, $J = 7.5$, 3H), 1.09 (d, $J = 7.5$, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 178.7, 135.1, 133.1, 129.5, 128.1, 58.5, 48.1, 33.1, 20.3, 18.61, 18.58, 18.45, 11.2, 10.9; IR (thin film) 3240, 1692 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{17}\text{H}_{29}\text{N}_2\text{OSi}$ ($\text{M} + \text{H}$)⁺ 305.2049, found 305.2055. Spectral data for **S20**: ^1H NMR (CDCl_3 , 400 MHz) δ 7.47 (m, 4H), 7.35 (m, 6H), 3.72 (m, 2H), 2.60 (m, 2H), 2.50–2.30 (m, 4H and m, 2H), 1.70 (m, 2H), 1.49–1.38 (m, 2H), 1.42–1.29 (m, 2H), 1.14–1.04 (m, 24H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 178.7, 135.1, 133.4, 129.4, 128.1, 56.4, 55.7, 33.5, 21.3, 18.7, 18.6, 18.5, 11.4, 11.0; IR (thin film) 3238, 1681, 1686 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{34}\text{H}_{53}\text{N}_3\text{NaO}_2\text{Si}_2$ ($\text{M} + \text{Na}$)⁺ 614.3574, found 614.3553.



N-Toluenesulfonamide S21. To a solution of **S19** (0.080 g, 0.26 mmol) and toluenesulfonyl chloride (0.065 g, 0.34 mmol) in CH_2Cl_2 (8 mL) at 24 °C was added Et_3N (0.050 mL, 0.34 mmol). The reaction mixture was stirred at 24 °C for 1 h. The reaction mixture was concentrated *in vacuo*, and diluted with saturated aqueous NH_4Cl (10 mL) and EtOAc (10 mL). The layers were separated, and the aqueous layer was extracted with EtOAc (3×10 mL). The combined organic layers were washed with saturated aqueous NaCl (20 mL). The resultant organic phase was dried with MgSO_4 and filtered. The filtrate was concentrated *in vacuo* to provide **S21** as a yellow oil. Purification by flash chromatography (80:20 to EtOAc) provided **S21** as a white crystalline solid (0.075 g, 62%): ^1H NMR (CDCl_3 , 500 MHz) δ 7.64 (d, $J = 8.2$, 2H), 7.38 (m, 5H), 7.29 (br s, 1H), 7.21 (d, $J = 8.1$, 2H), 6.81 (br s, 1H), 3.69 (m, 1H), 2.98 (m, 1H), 2.78 (m, 1H), 2.63 (dd, $J = 17.8$, 11.4, 1H), 2.39 (s, 3H), 2.32 (dd, $J = 17.8$, 7.2, 1H), 1.84 (m, 1H), 1.42–1.32 (m, 1H), 1.34–1.24 (m, 1H), 1.10–0.98 (m, 12H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 179.3, 143.3, 137.6, 135.1, 132.7, 129.8, 129.5, 128.2, 127.0, 56.5, 49.0, 32.8, 21.6, 19.8, 18.6, 18.5, 18.4, 18.3, 11.0, 10.7; IR (thin film) 3193, 1675, 1404, 1140 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{24}\text{H}_{34}\text{N}_2\text{NaO}_3\text{SSi}$ ($\text{M} + \text{Na}$) $^+$ 481.1957, found 481.1962. Anal. Calcd for $\text{C}_{24}\text{H}_{34}\text{N}_2\text{O}_3\text{SSi}$: C, 62.84; H, 7.47. Found: C, 62.92; H, 7.58.



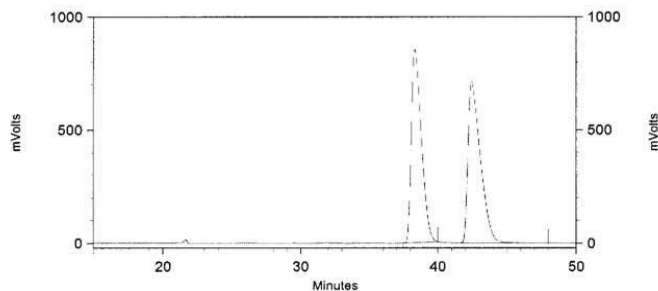
Lactam S22. To a solution of **S19** (0.010 g, 0.033 mmol) and DMAP (0.004 g, 0.04 mmol) in MeCN (0.5 mL) at 24 °C was added di-*tert*-butyl dicarbonate (0.01 mL, 0.05 mmol). The reaction mixture was stirred at 24 °C for 1 h. The reaction mixture was diluted with saturated aqueous NH_4Cl (3 mL). The layers were separated, and the aqueous layer was extracted with EtOAc (3×5 mL). The combined organic layers were washed with saturated aqueous NaCl (10 mL). The resultant organic phase was dried with Na_2SO_4 and filtered. The filtrate was concentrated *in vacuo* to afford unpurified **S22** as a colorless oil. Purification by flash chromatography (EtOAc) provided **S22** as a white solid (0.003 g, 22%, >95:5 diastereomer ratio as determined by ^1H NMR spectroscopy): ^1H NMR (CDCl_3 , 400 MHz) δ 7.44 (m, 5H), 4.26 (ddd, $J = 10.6$, 9.7, 7.9, 1H), 3.75 (dd, $J = 10.5$, 7.9, 1H), 3.39 (dd, $J = 10.5$, 9.7, 1H), 2.66 (m, 2H), 1.94 (ddd, $J = 12.5$, 10.7, 9.4, 1H), 1.51 (s, 9H), 1.35 (m, 2H), 1.18 (m, 12H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 172.7, 150.5, 135.1, 132.0, 130.2, 128.7, 83.9, 55.3, 50.2, 38.5, 28.2, 27.9, 19.0, 18.9, 18.8, 18.7, 11.8, 11.1; IR (thin film) 2946, 2867, 1818, 1713 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{22}\text{H}_{37}\text{N}_2\text{O}_3\text{Si}$ ($\text{M} + \text{H}$) $^+$ 405.2574, found 405.2571.

VI. HPLC Data for Enantioenriched α -Silyloxy Allylic Silane (-)-14

Page 1 of 1

Area % Report

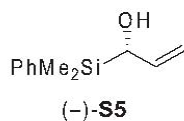
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Method: C:\Documents and Settings\User\Desktop\nick.met
Acquired: 10/16/2007 11:42:13 AM
Printed: 4/15/2008 3:20:37 PM

UV Detector
Ch1-254nm
Results

Retention Time	Area	Area %	Height	Height %
38.317	2265429	49.97	44068	54.91
40.833	302	0.01	38	0.05
42.442	2268093	50.03	36150	45.04
Totals	4533824	100.00	80256	100.00

UV Detector
Ch2-220nm
Results

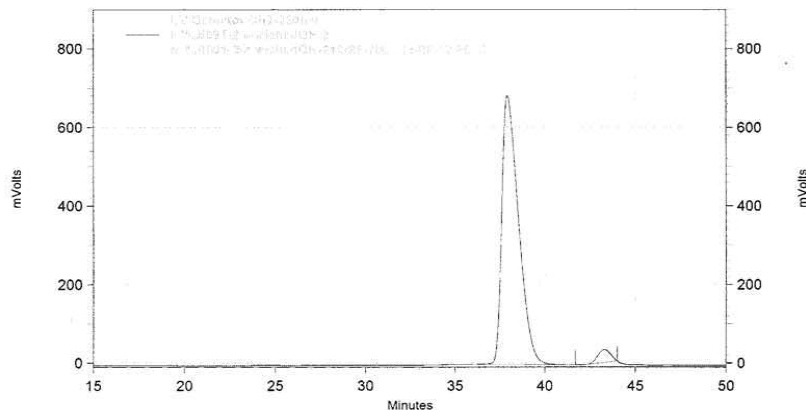
Retention Time	Area	Area %	Height	Height %
38.317	43277424	49.34	852690	54.59
42.442	44434722	50.66	709204	45.41
Totals	87712146	100.00	1561894	100.00



Page 1 of 1

Area % Report

Data File: C:\EZStart\Data\NML6091-2-enrichedOH-210-26-2007 11-02-12 PM.dat
Method: C:\EZStart\Methods\Chiracel Safe Methods\0.5%IPA hex-60 min w flush and
equilibration-special report NML.met
Acquired: 10/26/2007 11:03:02 PM
Printed: 10/27/2007 11:02:43 AM

**UV Detector
Ch1-254nm
Results**

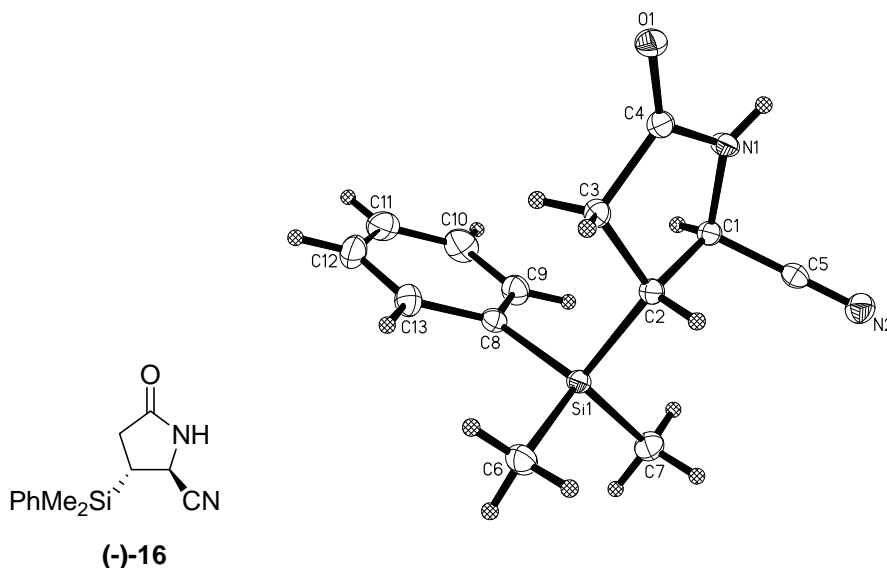
Retention Time	Area	Area %	Height	Height %
37.925	2237434	96.26	34754	95.12
43.292	86951	3.74	1784	4.88
Totals	2324385	100.00	36538	100.00

**UV Detector
Ch2-220nm
Results**

Retention Time	Area	Area %	Height	Height %
37.925	44152251	96.48	685341	95.38
43.292	1613012	3.52	33210	4.62
Totals	45765263	100.00	718551	100.00

VII. X-Ray Crystallography

X-ray Data Collection, Structure Solution and Refinement for Nitrile (–)-16.



A colorless crystal of approximate dimensions 0.09 x 0.26 x 0.28 mm was mounted on a glass fiber and transferred to a Bruker CCD platform diffractometer. The SMART¹ program package was used to determine the unit-cell parameters and for data collection (40 sec/frame scan time for a hemisphere of diffraction data). The raw frame data was processed using SAINT² and SADABS³ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL⁴ program. The diffraction symmetry was $2/m$ and the systematic absences were consistent with the centrosymmetric monoclinic space group $P2_1/c$ that was later determined to be correct.

The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors⁵ for neutral atoms were used throughout the analysis. Hydrogen atoms were located from a difference-Fourier map and refined (x, y, z and U_{iso}). At convergence, $wR2 = 0.1023$ and $Goof = 1.049$ for 218 variables refined against 3197 data (0.75\AA), $R1 = 0.0361$ for those 2530 data with $I > 2.0\sigma(I)$.

References.

1. SMART Software Users Guide, Version 5.1, Bruker Analytical X-Ray Systems, Inc.; Madison, WI 1999.
2. SAINT Software Users Guide, Version 6.0, Bruker Analytical X-Ray Systems, Inc.; Madison, WI 1999.
3. Sheldrick, G. M. SADABS, Version 2.10, Bruker Analytical X-Ray Systems, Inc.; Madison, WI 2002.
4. Sheldrick, G. M. SHELXTL Version 6.12, Bruker Analytical X-Ray Systems, Inc.; Madison, WI 2001.
5. International Tables for X-Ray Crystallography 1992, Vol. C., Dordrecht: Kluwer Academic Publishers.

Definitions:

$$wR2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}$$

$$R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$$

Goof = $S = [\Sigma [w(F_o^2 - F_c^2)^2] / (n-p)]^{1/2}$ where n is the number of reflections and p is the total number of parameters refined.

The thermal ellipsoid plot is shown at the 50% probability level.

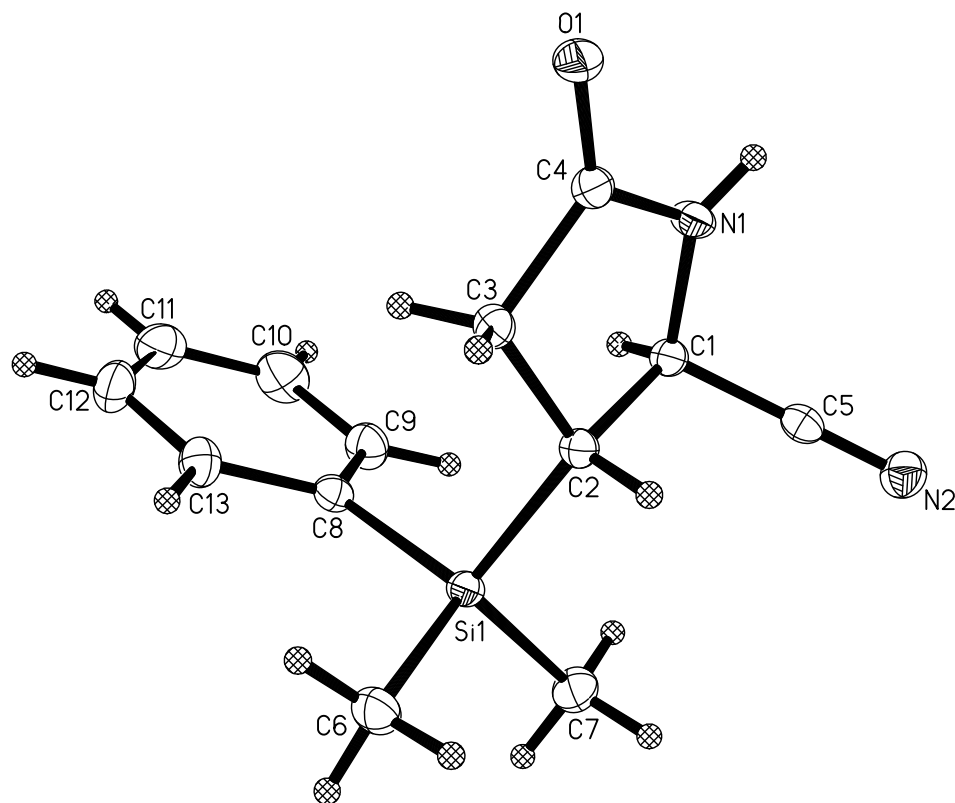


Table 1. Crystal data and structure refinement for nitrile (–)-**16**.

Identification code	kaw117 (Nick Leonard)
Empirical formula	C ₁₃ H ₁₆ N ₂ O Si
Formula weight	244.37
Temperature	155(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
Unit cell dimensions	$a = 15.1467(16) \text{ Å}$ $b = 6.6838(7) \text{ Å}$ $c = 12.8779(13) \text{ Å}$
	$\alpha = 90^\circ$ $\beta = 90.948(2)^\circ$ $\gamma = 90^\circ$
Volume	1303.5(2) Å ³
<i>Z</i>	4
Density (calculated)	1.245 Mg/m ³

Absorption coefficient	0.166 mm ⁻¹
F(000)	520
Crystal color	colorless
Crystal size	0.28 x 0.26 x 0.09 mm ³
Theta range for data collection	2.69 to 28.29°.
Index ranges	-20 ≤ <i>h</i> ≤ 20, -8 ≤ <i>k</i> ≤ 8, -17 ≤ <i>l</i> ≤ 14
Reflections collected	8489
Independent reflections	3197 [R(int) = 0.0284]
Completeness to theta = 28.29°	98.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9852 and 0.9550
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3197 / 0 / 218
Goodness-of-fit on F ²	1.049
Final R indices [I>2sigma(I) = 2530 data]	R1 = 0.0361, wR2 = 0.0918
R indices (all data, 0.75Å)	R1 = 0.0519, wR2 = 0.1023
Largest diff. peak and hole	0.541 and -0.259 e.Å ⁻³

Table 2. Atomic coordinates (x 10⁴) and equivalent isotropic displacement parameters (Å²x 10³) for nitrile (–)-**16**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Si(1)	2489(1)	1373(1)	9013(1)	13(1)
O(1)	990(1)	-4720(2)	10892(1)	20(1)
N(1)	622(1)	-2952(2)	9419(1)	17(1)
N(2)	-285(1)	799(2)	7933(1)	22(1)
C(1)	980(1)	-1335(2)	8791(1)	14(1)
C(2)	1550(1)	-114(2)	9583(1)	14(1)
C(3)	1819(1)	-1735(2)	10377(1)	16(1)
C(4)	1102(1)	-3313(2)	10291(1)	16(1)
C(5)	266(1)	-135(2)	8311(1)	16(1)
C(6)	2974(1)	2934(2)	10078(1)	22(1)
C(7)	2067(1)	2965(2)	7930(1)	23(1)
C(8)	3322(1)	-478(2)	8534(1)	16(1)
C(9)	3235(1)	-1354(2)	7551(1)	22(1)
C(10)	3813(1)	-2824(3)	7222(1)	30(1)
C(11)	4494(1)	-3474(3)	7869(2)	30(1)

C(12)	4598(1)	-2635(3)	8846(1)	28(1)
C(13)	4025(1)	-1149(2)	9169(1)	21(1)

Table 3. Bond lengths [Å] and angles [°] for nitrile (–)-**16**.

Si(1)-C(7)	1.8597(15)
Si(1)-C(6)	1.8644(15)
Si(1)-C(8)	1.8784(14)
Si(1)-C(2)	1.8932(14)
O(1)-C(4)	1.2320(17)
N(1)-C(4)	1.3489(18)
N(1)-C(1)	1.4596(18)
N(2)-C(5)	1.1435(18)
C(1)-C(5)	1.4747(19)
C(1)-C(2)	1.5570(18)
C(2)-C(3)	1.5397(18)
C(3)-C(4)	1.5169(19)
C(8)-C(9)	1.399(2)
C(8)-C(13)	1.405(2)
C(9)-C(10)	1.387(2)
C(10)-C(11)	1.385(3)
C(11)-C(12)	1.384(3)
C(12)-C(13)	1.388(2)
C(7)-Si(1)-C(6)	110.99(8)
C(7)-Si(1)-C(8)	110.80(7)
C(6)-Si(1)-C(8)	110.58(7)
C(7)-Si(1)-C(2)	109.89(7)
C(6)-Si(1)-C(2)	107.31(7)
C(8)-Si(1)-C(2)	107.13(6)
C(4)-N(1)-C(1)	113.16(12)
N(1)-C(1)-C(5)	111.02(11)
N(1)-C(1)-C(2)	103.46(10)
C(5)-C(1)-C(2)	112.68(11)
C(3)-C(2)-C(1)	101.75(10)
C(3)-C(2)-Si(1)	115.80(9)
C(1)-C(2)-Si(1)	115.68(9)
C(4)-C(3)-C(2)	105.05(11)

O(1)-C(4)-N(1)	125.58(13)
O(1)-C(4)-C(3)	126.19(13)
N(1)-C(4)-C(3)	108.19(12)
N(2)-C(5)-C(1)	179.56(16)
C(9)-C(8)-C(13)	116.90(13)
C(9)-C(8)-Si(1)	121.27(11)
C(13)-C(8)-Si(1)	121.70(11)
C(10)-C(9)-C(8)	121.49(15)
C(11)-C(10)-C(9)	120.42(16)
C(12)-C(11)-C(10)	119.46(15)
C(11)-C(12)-C(13)	120.02(15)
C(12)-C(13)-C(8)	121.70(14)

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for nitrile (–)-**16**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
Si(1)	14(1)	12(1)	14(1)	1(1)	-1(1)	-1(1)
O(1)	21(1)	19(1)	22(1)	7(1)	-2(1)	-2(1)
N(1)	18(1)	15(1)	17(1)	3(1)	-4(1)	-5(1)
N(2)	22(1)	21(1)	21(1)	1(1)	-4(1)	1(1)
C(1)	15(1)	14(1)	13(1)	1(1)	-1(1)	-1(1)
C(2)	14(1)	14(1)	12(1)	0(1)	-1(1)	-1(1)
C(3)	16(1)	18(1)	14(1)	4(1)	-2(1)	-2(1)
C(4)	15(1)	15(1)	17(1)	1(1)	1(1)	0(1)
C(5)	17(1)	16(1)	13(1)	-1(1)	0(1)	-4(1)
C(6)	20(1)	20(1)	25(1)	-6(1)	-1(1)	-2(1)
C(7)	23(1)	21(1)	25(1)	8(1)	-1(1)	1(1)
C(8)	15(1)	15(1)	16(1)	1(1)	2(1)	-2(1)
C(9)	22(1)	24(1)	21(1)	-4(1)	-3(1)	-1(1)
C(10)	31(1)	30(1)	29(1)	-13(1)	4(1)	-2(1)
C(11)	24(1)	21(1)	47(1)	-5(1)	10(1)	3(1)
C(12)	19(1)	28(1)	37(1)	7(1)	-1(1)	5(1)
C(13)	19(1)	26(1)	19(1)	2(1)	-1(1)	0(1)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for nitrile (–)-**16**.

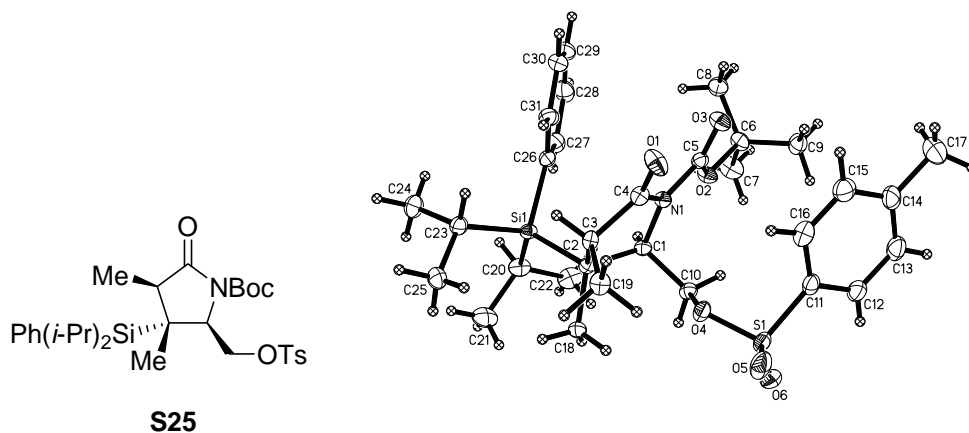
	x	y	z	U(eq)
H(1)	198(12)	-3700(30)	9229(14)	28(5)
H(1A)	1328(10)	-1850(20)	8245(12)	12(4)
H(2A)	1150(11)	780(20)	9919(13)	19(4)
H(3A)	2379(11)	-2350(30)	10204(13)	21(4)
H(3B)	1831(11)	-1220(30)	11080(14)	21(4)
H(6A)	2522(14)	3720(30)	10364(15)	37(5)
H(6B)	3271(13)	2150(30)	10632(15)	38(5)
H(6C)	3409(15)	3850(30)	9830(16)	45(6)
H(7A)	1823(13)	2170(30)	7368(15)	35(5)
H(7B)	2528(14)	3780(30)	7685(15)	38(6)
H(7C)	1618(15)	3840(30)	8148(16)	46(6)
H(9A)	2765(12)	-930(30)	7116(14)	30(5)
H(10A)	3746(13)	-3380(30)	6565(16)	39(6)
H(11A)	4889(13)	-4470(30)	7646(15)	36(5)
H(12A)	5058(13)	-3080(30)	9285(14)	31(5)
H(13A)	4106(12)	-510(30)	9840(15)	31(5)

Table 6. Torsion angles [$^{\circ}$] for nitrile (–)-**16**.

C(4)-N(1)-C(1)-C(5)	-143.18(12)
C(4)-N(1)-C(1)-C(2)	-22.07(15)
N(1)-C(1)-C(2)-C(3)	28.11(13)
C(5)-C(1)-C(2)-C(3)	148.08(11)
N(1)-C(1)-C(2)-Si(1)	154.50(9)
C(5)-C(1)-C(2)-Si(1)	-85.53(13)
C(7)-Si(1)-C(2)-C(3)	171.13(10)
C(6)-Si(1)-C(2)-C(3)	-68.09(12)
C(8)-Si(1)-C(2)-C(3)	50.68(11)
C(7)-Si(1)-C(2)-C(1)	52.22(12)
C(6)-Si(1)-C(2)-C(1)	172.99(10)
C(8)-Si(1)-C(2)-C(1)	-68.23(11)
C(1)-C(2)-C(3)-C(4)	-25.33(13)
Si(1)-C(2)-C(3)-C(4)	-151.64(9)
C(1)-N(1)-C(4)-O(1)	-172.31(13)

C(1)-N(1)-C(4)-C(3)	5.65(16)
C(2)-C(3)-C(4)-O(1)	-168.56(14)
C(2)-C(3)-C(4)-N(1)	13.50(15)
N(1)-C(1)-C(5)-N(2)	-154(100)
C(2)-C(1)-C(5)-N(2)	90(24)
C(7)-Si(1)-C(8)-C(9)	-35.57(14)
C(6)-Si(1)-C(8)-C(9)	-159.07(12)
C(2)-Si(1)-C(8)-C(9)	84.30(13)
C(7)-Si(1)-C(8)-C(13)	148.84(12)
C(6)-Si(1)-C(8)-C(13)	25.34(14)
C(2)-Si(1)-C(8)-C(13)	-91.29(13)
C(13)-C(8)-C(9)-C(10)	0.4(2)
Si(1)-C(8)-C(9)-C(10)	-175.41(13)
C(8)-C(9)-C(10)-C(11)	0.3(3)
C(9)-C(10)-C(11)-C(12)	-0.4(3)
C(10)-C(11)-C(12)-C(13)	-0.3(3)
C(11)-C(12)-C(13)-C(8)	1.0(2)
C(9)-C(8)-C(13)-C(12)	-1.1(2)
Si(1)-C(8)-C(13)-C(12)	174.71(12)

X-ray Data Collection, Structure Solution and Refinement for Tosylate **S25**.
 Note: Compound **S25** is an intermediate in the formation of δ -lactam **4** (Scheme 1.)



A colorless crystal of approximate dimensions 0.21 x 0.26 x 0.34 mm was mounted on a glass fiber and transferred to a Bruker CCD platform diffractometer. The SMART¹ program package was used to determine the unit-cell parameters and for data collection (25 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT² and SADABS³ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL⁴ program. The diffraction symmetry was *mmm* and the systematic absences were consistent with the orthorhombic space groups *Pna2*₁ and *Pnma*. It was later determined that the noncentrosymmetric space group *Pna2*₁ was correct.

The structure was solved by direct methods and refined on *F*² by full-matrix least-squares techniques. The analytical scattering factors⁵ for neutral atoms were used throughout the analysis. Hydrogen atoms were located from a difference-Fourier map and refined (*x*,*y*,*z* and *U*_{iso}). At convergence, *wR*2 = 0.0720 and GOF = 1.056 for 541 variables refined against 7744 data (0.75Å), *R*1 = 0.0301 for those 6796 data with *I* > 2.0σ(*I*). The absolute structure was assigned by refinement of the Flack⁶ parameter.

References.

1. SMART Software Users Guide, Version 5.1, Bruker Analytical X-Ray Systems, Inc.; Madison, WI 1999.
2. SAINT Software Users Guide, Version 6.0, Bruker Analytical X-Ray Systems, Inc.; Madison, WI 1999.
3. Sheldrick, G. M. SADABS, Version 2.10, Bruker Analytical X-Ray Systems, Inc.; Madison, WI 2002.
4. Sheldrick, G. M. SHELXTL Version 6.12, Bruker Analytical X-Ray Systems, Inc.; Madison, WI 2001.
5. International Tables for X-Ray Crystallography 1992, Vol. C., Dordrecht: Kluwer Academic Publishers.
6. Flack, H. D. Acta. Cryst., A39, 876-881, 1983.

Definitions:

$$wR2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)]]^{1/2}$$

$$R1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$$

$$Goof = S = [\Sigma[w(F_o^2 - F_c^2)^2] / (n-p)]^{1/2} \text{ where } n \text{ is the number of reflections and } p \text{ is the total}$$

number of parameters refined.

The thermal ellipsoid plot is shown at the 50% probability level.

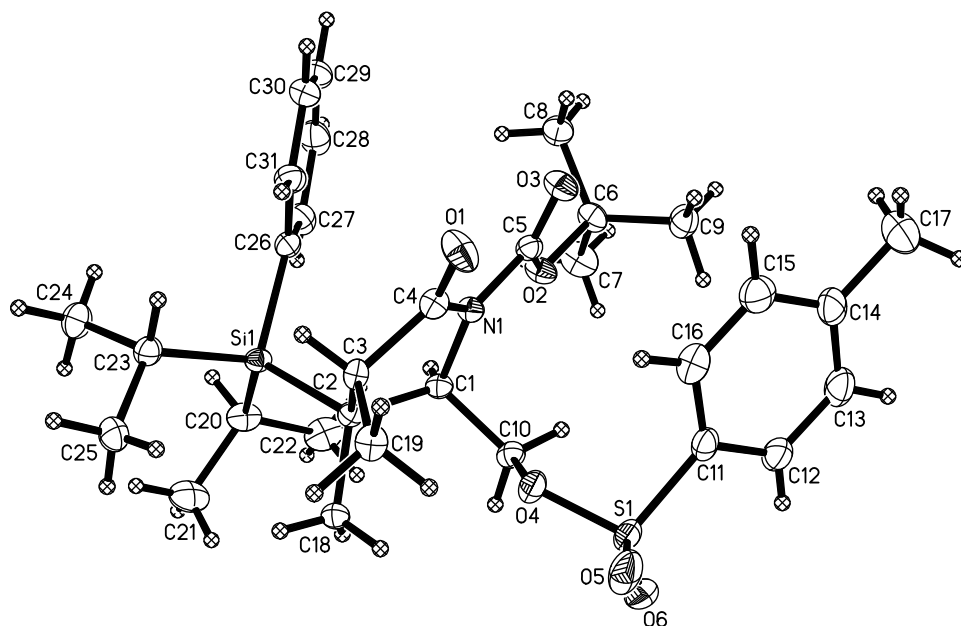


Table 1. Crystal data and structure refinement for tosylate **S25**.

Identification code	kaw103 (Nick Leonard)	
Empirical formula	$C_{31} H_{45} N O_6 S Si$	
Formula weight	587.83	
Temperature	158(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$Pna2_1$	
Unit cell dimensions	$a = 19.3855(16)$ Å	$\alpha = 90^\circ$.
	$b = 9.3470(8)$ Å	$\beta = 90^\circ$.
	$c = 17.3356(14)$ Å	$\gamma = 90^\circ$.
Volume	$3141.1(5)$ Å ³	
Z	4	
Density (calculated)	1.243 Mg/m ³	
Absorption coefficient	0.184 mm ⁻¹	
F(000)	1264	
Crystal color	colorless	
Crystal size	$0.34 \times 0.26 \times 0.21$ mm ³	
Theta range for data collection	2.10 to 28.33°	
Index ranges	$-25 \leq h \leq 25$, $-12 \leq k \leq 12$, $-23 \leq l \leq 23$	

Reflections collected	33302
Independent reflections	7744 [R(int) = 0.0405]
Completeness to theta = 28.33°	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9625 and 0.9402
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	7744 / 1 / 541
Goodness-of-fit on F ²	1.056
Final R indices [I>2sigma(I) = 6796 data]	R1 = 0.0301, wR2 = 0.0666
R indices (all data, 0.75Å)	R1 = 0.0416, wR2 = 0.0720
Absolute structure parameter	-0.04(5)
Largest diff. peak and hole	0.293 and -0.228 e.Å ⁻³

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for tosylate **S25**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(1)	11895(1)	7187(1)	6771(1)	26(1)
Si(1)	9298(1)	3047(1)	6355(1)	16(1)
O(1)	9964(1)	7048(1)	4887(1)	29(1)
O(2)	11293(1)	3512(1)	4857(1)	20(1)
O(3)	10897(1)	5322(1)	4099(1)	23(1)
O(4)	11212(1)	6304(1)	6632(1)	22(1)
O(5)	11648(1)	8571(2)	6983(1)	38(1)
O(6)	12335(1)	6409(2)	7283(1)	36(1)
N(1)	10535(1)	5047(1)	5355(1)	16(1)
C(1)	10604(1)	4303(2)	6096(1)	16(1)
C(2)	9915(1)	4636(2)	6528(1)	15(1)
C(3)	9643(1)	6016(2)	6124(1)	16(1)
C(4)	10049(1)	6140(2)	5374(1)	18(1)
C(5)	10918(1)	4681(2)	4693(1)	17(1)
C(6)	11725(1)	2829(2)	4246(1)	22(1)
C(7)	11986(1)	1501(2)	4654(1)	33(1)
C(8)	11279(1)	2420(2)	3568(1)	26(1)
C(9)	12310(1)	3830(2)	4040(1)	27(1)
C(10)	11270(1)	4772(2)	6492(1)	19(1)
C(11)	12273(1)	7253(2)	5849(1)	22(1)

C(12)	12970(1)	6942(2)	5773(1)	27(1)
C(13)	13279(1)	7076(2)	5057(1)	33(1)
C(14)	12898(1)	7490(2)	4415(1)	31(1)
C(15)	12196(1)	7765(2)	4505(1)	32(1)
C(16)	11884(1)	7662(2)	5217(1)	28(1)
C(17)	13239(2)	7619(3)	3634(2)	51(1)
C(18)	10014(1)	4798(2)	7404(1)	19(1)
C(19)	9680(1)	7436(2)	6564(1)	21(1)
C(20)	9545(1)	1438(2)	6969(1)	24(1)
C(21)	9289(1)	1475(2)	7810(1)	33(1)
C(22)	10313(1)	1037(2)	6954(1)	31(1)
C(23)	8362(1)	3574(2)	6511(1)	21(1)
C(24)	7895(1)	2235(2)	6482(1)	31(1)
C(25)	8193(1)	4477(2)	7223(1)	25(1)
C(26)	9327(1)	2497(2)	5303(1)	19(1)
C(27)	9557(1)	1151(2)	5060(1)	26(1)
C(28)	9521(1)	733(2)	4293(1)	32(1)
C(29)	9255(1)	1658(2)	3744(1)	32(1)
C(30)	9030(1)	3002(2)	3965(1)	29(1)
C(31)	9065(1)	3414(2)	4733(1)	23(1)

Table 3. Bond lengths [Å] and angles [°] for tosylate **S25**.

S(1)-O(5)	1.4274(14)
S(1)-O(6)	1.4299(14)
S(1)-O(4)	1.5777(11)
S(1)-C(11)	1.7609(17)
Si(1)-C(26)	1.8962(16)
Si(1)-C(23)	1.8991(16)
Si(1)-C(20)	1.9030(16)
Si(1)-C(2)	1.9304(15)
O(1)-C(4)	1.2081(19)
O(2)-C(5)	1.3418(18)
O(2)-C(6)	1.4934(18)
O(3)-C(5)	1.1927(18)
O(4)-C(10)	1.4574(19)
N(1)-C(4)	1.3898(19)
N(1)-C(5)	1.4094(19)

N(1)-C(1)	1.4681(19)
C(1)-C(10)	1.526(2)
C(1)-C(2)	1.563(2)
C(2)-C(18)	1.539(2)
C(2)-C(3)	1.559(2)
C(3)-C(4)	1.525(2)
C(3)-C(19)	1.532(2)
C(6)-C(8)	1.510(2)
C(6)-C(9)	1.514(2)
C(6)-C(7)	1.515(2)
C(11)-C(16)	1.384(3)
C(11)-C(12)	1.388(2)
C(12)-C(13)	1.384(3)
C(13)-C(14)	1.391(3)
C(14)-C(15)	1.394(3)
C(14)-C(17)	1.511(3)
C(15)-C(16)	1.377(3)
C(20)-C(22)	1.536(3)
C(20)-C(21)	1.541(3)
C(23)-C(25)	1.530(2)
C(23)-C(24)	1.545(2)
C(26)-C(27)	1.400(2)
C(26)-C(31)	1.403(2)
C(27)-C(28)	1.387(3)
C(28)-C(29)	1.386(3)
C(29)-C(30)	1.384(3)
C(30)-C(31)	1.387(2)
O(5)-S(1)-O(6)	120.13(9)
O(5)-S(1)-O(4)	103.43(7)
O(6)-S(1)-O(4)	109.23(7)
O(5)-S(1)-C(11)	109.99(9)
O(6)-S(1)-C(11)	109.37(8)
O(4)-S(1)-C(11)	103.24(7)
C(26)-Si(1)-C(23)	103.66(7)
C(26)-Si(1)-C(20)	108.42(7)
C(23)-Si(1)-C(20)	111.46(7)
C(26)-Si(1)-C(2)	109.80(7)

C(23)-Si(1)-C(2)	111.70(7)
C(20)-Si(1)-C(2)	111.46(7)
C(5)-O(2)-C(6)	120.13(12)
C(10)-O(4)-S(1)	118.38(9)
C(4)-N(1)-C(5)	123.75(13)
C(4)-N(1)-C(1)	112.95(12)
C(5)-N(1)-C(1)	123.30(12)
N(1)-C(1)-C(10)	109.64(12)
N(1)-C(1)-C(2)	104.23(11)
C(10)-C(1)-C(2)	116.81(13)
C(18)-C(2)-C(3)	113.82(12)
C(18)-C(2)-C(1)	112.63(12)
C(3)-C(2)-C(1)	103.82(11)
C(18)-C(2)-Si(1)	107.83(10)
C(3)-C(2)-Si(1)	110.99(9)
C(1)-C(2)-Si(1)	107.60(10)
C(4)-C(3)-C(19)	109.52(12)
C(4)-C(3)-C(2)	105.77(11)
C(19)-C(3)-C(2)	118.53(13)
O(1)-C(4)-N(1)	126.30(14)
O(1)-C(4)-C(3)	125.41(14)
N(1)-C(4)-C(3)	108.29(12)
O(3)-C(5)-O(2)	127.61(14)
O(3)-C(5)-N(1)	124.26(14)
O(2)-C(5)-N(1)	108.13(12)
O(2)-C(6)-C(8)	109.83(13)
O(2)-C(6)-C(9)	108.86(13)
C(8)-C(6)-C(9)	113.69(15)
O(2)-C(6)-C(7)	101.98(13)
C(8)-C(6)-C(7)	110.34(16)
C(9)-C(6)-C(7)	111.50(15)
O(4)-C(10)-C(1)	106.98(12)
C(16)-C(11)-C(12)	120.93(17)
C(16)-C(11)-S(1)	120.09(12)
C(12)-C(11)-S(1)	118.94(14)
C(13)-C(12)-C(11)	119.15(18)
C(12)-C(13)-C(14)	120.87(17)
C(13)-C(14)-C(15)	118.68(17)

C(13)-C(14)-C(17)	120.4(2)
C(15)-C(14)-C(17)	120.9(2)
C(16)-C(15)-C(14)	121.07(18)
C(15)-C(16)-C(11)	119.27(16)
C(22)-C(20)-C(21)	109.49(15)
C(22)-C(20)-Si(1)	115.30(12)
C(21)-C(20)-Si(1)	115.47(13)
C(25)-C(23)-C(24)	110.37(14)
C(25)-C(23)-Si(1)	117.53(11)
C(24)-C(23)-Si(1)	110.16(12)
C(27)-C(26)-C(31)	116.86(15)
C(27)-C(26)-Si(1)	122.88(13)
C(31)-C(26)-Si(1)	120.10(12)
C(28)-C(27)-C(26)	121.73(17)
C(29)-C(28)-C(27)	120.12(18)
C(30)-C(29)-C(28)	119.51(16)
C(29)-C(30)-C(31)	120.16(18)
C(30)-C(31)-C(26)	121.62(17)

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for tosylate **S25**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
S(1)	16(1)	33(1)	27(1)	-11(1)	1(1)	-6(1)
Si(1)	19(1)	13(1)	15(1)	0(1)	-1(1)	-2(1)
O(1)	30(1)	27(1)	29(1)	12(1)	9(1)	11(1)
O(2)	24(1)	21(1)	17(1)	-1(1)	3(1)	8(1)
O(3)	27(1)	25(1)	18(1)	3(1)	3(1)	6(1)
O(4)	16(1)	22(1)	28(1)	-7(1)	0(1)	-2(1)
O(5)	27(1)	37(1)	51(1)	-25(1)	10(1)	-10(1)
O(6)	22(1)	60(1)	25(1)	-5(1)	-5(1)	-6(1)
N(1)	16(1)	16(1)	15(1)	0(1)	0(1)	2(1)
C(1)	17(1)	15(1)	15(1)	1(1)	-2(1)	2(1)
C(2)	15(1)	14(1)	15(1)	-1(1)	0(1)	0(1)
C(3)	14(1)	15(1)	21(1)	0(1)	1(1)	0(1)
C(4)	18(1)	16(1)	21(1)	1(1)	-2(1)	1(1)

C(5)	16(1)	18(1)	17(1)	-3(1)	-1(1)	0(1)
C(6)	22(1)	22(1)	21(1)	-4(1)	5(1)	6(1)
C(7)	39(1)	26(1)	34(1)	-1(1)	5(1)	13(1)
C(8)	27(1)	28(1)	24(1)	-8(1)	3(1)	-1(1)
C(9)	21(1)	30(1)	31(1)	-3(1)	2(1)	0(1)
C(10)	16(1)	20(1)	19(1)	-1(1)	-2(1)	3(1)
C(11)	19(1)	20(1)	27(1)	-5(1)	2(1)	-5(1)
C(12)	19(1)	34(1)	29(1)	-5(1)	-1(1)	-2(1)
C(13)	20(1)	39(1)	39(1)	-11(1)	6(1)	-5(1)
C(14)	34(1)	27(1)	32(1)	-3(1)	6(1)	-13(1)
C(15)	35(1)	28(1)	33(1)	4(1)	-5(1)	-7(1)
C(16)	23(1)	23(1)	38(1)	0(1)	-1(1)	-1(1)
C(17)	54(2)	65(2)	35(1)	-2(1)	12(1)	-19(1)
C(18)	20(1)	19(1)	16(1)	-3(1)	1(1)	-1(1)
C(19)	21(1)	15(1)	28(1)	-1(1)	2(1)	2(1)
C(20)	34(1)	15(1)	22(1)	3(1)	-4(1)	-1(1)
C(21)	48(1)	26(1)	23(1)	9(1)	-2(1)	-3(1)
C(22)	38(1)	19(1)	34(1)	4(1)	-8(1)	4(1)
C(23)	21(1)	21(1)	21(1)	1(1)	-1(1)	-4(1)
C(24)	28(1)	31(1)	33(1)	-1(1)	2(1)	-14(1)
C(25)	21(1)	29(1)	27(1)	-2(1)	4(1)	2(1)
C(26)	20(1)	20(1)	18(1)	-4(1)	1(1)	-6(1)
C(27)	27(1)	24(1)	26(1)	-3(1)	4(1)	-4(1)
C(28)	33(1)	32(1)	30(1)	-13(1)	9(1)	-7(1)
C(29)	31(1)	46(1)	19(1)	-12(1)	5(1)	-10(1)
C(30)	27(1)	40(1)	18(1)	1(1)	0(1)	-7(1)
C(31)	26(1)	23(1)	20(1)	-1(1)	-1(1)	-4(1)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for tosylate **S25**.

	x	y	z	U(eq)
H(1A)	10665(9)	3320(20)	5996(11)	20(4)
H(3A)	9180(9)	5859(19)	5932(10)	16(4)
H(7A)	11626(11)	870(20)	4818(13)	39(6)
H(7B)	12235(13)	1780(30)	5073(15)	45(7)
H(7C)	12278(12)	950(20)	4303(13)	41(6)
H(8A)	10907(11)	1880(20)	3743(12)	26(5)

H(8B)	11524(11)	1830(20)	3212(14)	38(6)
H(8C)	11110(12)	3260(30)	3290(14)	46(6)
H(9A)	12142(10)	4710(20)	3827(11)	24(5)
H(9B)	12582(11)	4060(20)	4500(12)	34(5)
H(9C)	12613(13)	3320(30)	3656(15)	53(7)
H(10A)	11664(9)	4560(19)	6166(11)	21(5)
H(10B)	11357(10)	4320(20)	6982(12)	25(5)
H(12)	13200(10)	6710(20)	6177(12)	29(5)
H(13)	13770(11)	6870(20)	5014(12)	34(6)
H(15)	11924(12)	8060(20)	4056(15)	42(6)
H(16)	11422(12)	7880(20)	5296(12)	34(5)
H(17A)	13184(18)	6710(40)	3370(20)	95(11)
H(17B)	13713(15)	7910(30)	3700(16)	59(8)
H(17C)	12968(17)	8260(40)	3360(20)	83(11)
H(18A)	10303(9)	5620(20)	7518(11)	22(5)
H(18B)	10241(9)	4020(19)	7602(10)	14(4)
H(18C)	9604(10)	4910(19)	7638(11)	19(4)
H(19A)	9539(9)	8212(19)	6232(11)	20(4)
H(19B)	9382(10)	7420(20)	7074(13)	32(5)
H(19C)	10161(10)	7680(20)	6780(12)	29(5)
H(20A)	9291(8)	630(20)	6730(10)	17(4)
H(21A)	8811(12)	1670(20)	7820(12)	30(5)
H(21B)	9481(11)	2190(20)	8091(13)	34(6)
H(21C)	9354(12)	540(30)	8038(14)	53(7)
H(22A)	10591(10)	1720(20)	7205(12)	26(5)
H(22B)	10506(9)	975(19)	6433(12)	21(4)
H(22C)	10360(11)	160(20)	7241(12)	38(6)
H(23A)	8259(9)	4110(20)	6043(11)	20(4)
H(24A)	7974(11)	1660(20)	6047(13)	35(5)
H(24B)	7395(13)	2610(20)	6492(14)	50(7)
H(24C)	7980(10)	1550(20)	6956(13)	34(5)
H(25A)	8315(10)	4010(20)	7701(12)	22(5)
H(25B)	8431(10)	5370(20)	7193(11)	24(5)
H(25C)	7713(12)	4640(20)	7228(13)	41(6)
H(27)	9725(10)	434(19)	5451(11)	22(5)
H(28)	9665(11)	-160(20)	4139(13)	39(6)
H(29)	9238(10)	1360(20)	3231(13)	32(5)
H(30)	8849(12)	3680(20)	3593(14)	46(6)

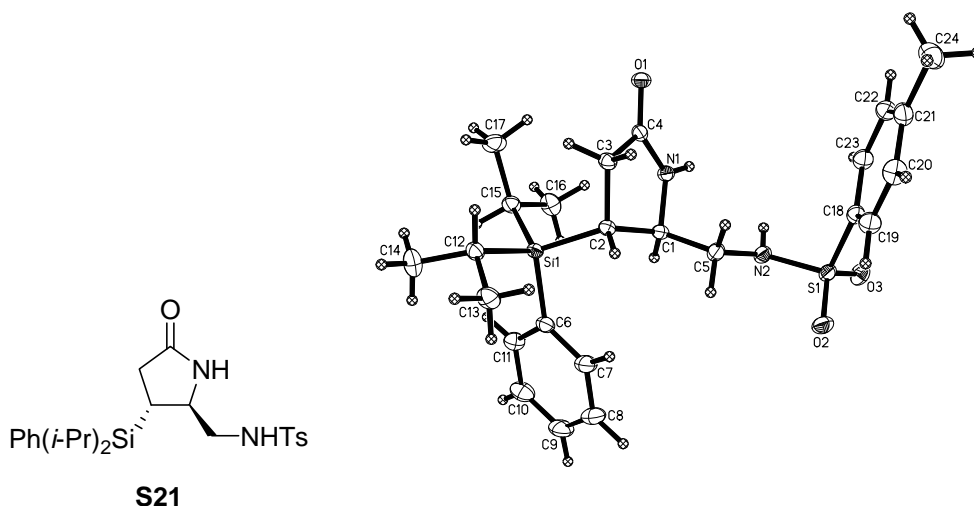
H(31)	8914(9)	4310(20)	4855(10)	17(4)
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Table 6. Torsion angles [°] for tosylate **S25**.

O(5)-S(1)-O(4)-C(10)	-172.85(11)
O(6)-S(1)-O(4)-C(10)	-43.82(13)
C(11)-S(1)-O(4)-C(10)	72.48(12)
C(4)-N(1)-C(1)-C(10)	-104.73(14)
C(5)-N(1)-C(1)-C(10)	75.69(17)
C(4)-N(1)-C(1)-C(2)	21.04(16)
C(5)-N(1)-C(1)-C(2)	-158.54(12)
N(1)-C(1)-C(2)-C(18)	-145.23(12)
C(10)-C(1)-C(2)-C(18)	-24.13(18)
N(1)-C(1)-C(2)-C(3)	-21.65(14)
C(10)-C(1)-C(2)-C(3)	99.45(14)
N(1)-C(1)-C(2)-Si(1)	96.07(11)
C(10)-C(1)-C(2)-Si(1)	-142.83(11)
C(26)-Si(1)-C(2)-C(18)	-165.99(10)
C(23)-Si(1)-C(2)-C(18)	79.59(12)
C(20)-Si(1)-C(2)-C(18)	-45.82(12)
C(26)-Si(1)-C(2)-C(3)	68.71(11)
C(23)-Si(1)-C(2)-C(3)	-45.71(12)
C(20)-Si(1)-C(2)-C(3)	-171.13(10)
C(26)-Si(1)-C(2)-C(1)	-44.25(11)
C(23)-Si(1)-C(2)-C(1)	-158.67(9)
C(20)-Si(1)-C(2)-C(1)	75.91(11)
C(18)-C(2)-C(3)-C(4)	138.61(13)
C(1)-C(2)-C(3)-C(4)	15.82(14)
Si(1)-C(2)-C(3)-C(4)	-99.52(11)
C(18)-C(2)-C(3)-C(19)	15.33(18)
C(1)-C(2)-C(3)-C(19)	-107.47(14)
Si(1)-C(2)-C(3)-C(19)	137.20(12)
C(5)-N(1)-C(4)-O(1)	-12.2(2)
C(1)-N(1)-C(4)-O(1)	168.21(16)
C(5)-N(1)-C(4)-C(3)	168.56(13)
C(1)-N(1)-C(4)-C(3)	-11.02(16)
C(19)-C(3)-C(4)-O(1)	-54.4(2)
C(2)-C(3)-C(4)-O(1)	176.83(15)
C(19)-C(3)-C(4)-N(1)	124.88(13)

C(2)-C(3)-C(4)-N(1)	-3.93(15)
C(6)-O(2)-C(5)-O(3)	-2.9(2)
C(6)-O(2)-C(5)-N(1)	176.75(12)
C(4)-N(1)-C(5)-O(3)	4.8(2)
C(1)-N(1)-C(5)-O(3)	-175.63(14)
C(4)-N(1)-C(5)-O(2)	-174.87(13)
C(1)-N(1)-C(5)-O(2)	4.67(19)
C(5)-O(2)-C(6)-C(8)	-57.30(18)
C(5)-O(2)-C(6)-C(9)	67.76(17)
C(5)-O(2)-C(6)-C(7)	-174.31(14)
S(1)-O(4)-C(10)-C(1)	-159.67(10)
N(1)-C(1)-C(10)-O(4)	61.84(15)
C(2)-C(1)-C(10)-O(4)	-56.37(17)
O(5)-S(1)-C(11)-C(16)	-60.49(16)
O(6)-S(1)-C(11)-C(16)	165.55(14)
O(4)-S(1)-C(11)-C(16)	49.36(15)
O(5)-S(1)-C(11)-C(12)	117.13(15)
O(6)-S(1)-C(11)-C(12)	-16.83(17)
O(4)-S(1)-C(11)-C(12)	-133.02(14)
C(16)-C(11)-C(12)-C(13)	1.4(3)
S(1)-C(11)-C(12)-C(13)	-176.15(14)
C(11)-C(12)-C(13)-C(14)	-1.2(3)
C(12)-C(13)-C(14)-C(15)	-0.2(3)
C(12)-C(13)-C(14)-C(17)	-179.4(2)
C(13)-C(14)-C(15)-C(16)	1.4(3)
C(17)-C(14)-C(15)-C(16)	-179.4(2)
C(14)-C(15)-C(16)-C(11)	-1.1(3)
C(12)-C(11)-C(16)-C(15)	-0.3(3)
S(1)-C(11)-C(16)-C(15)	177.27(14)
C(26)-Si(1)-C(20)-C(22)	73.32(14)
C(23)-Si(1)-C(20)-C(22)	-173.20(12)
C(2)-Si(1)-C(20)-C(22)	-47.66(15)
C(26)-Si(1)-C(20)-C(21)	-157.34(13)
C(23)-Si(1)-C(20)-C(21)	-43.86(16)
C(2)-Si(1)-C(20)-C(21)	81.68(15)
C(26)-Si(1)-C(23)-C(25)	-162.64(13)
C(20)-Si(1)-C(23)-C(25)	80.94(14)
C(2)-Si(1)-C(23)-C(25)	-44.47(14)

C(26)-Si(1)-C(23)-C(24)	69.81(13)
C(20)-Si(1)-C(23)-C(24)	-46.61(14)
C(2)-Si(1)-C(23)-C(24)	-172.02(11)
C(23)-Si(1)-C(26)-C(27)	-123.60(14)
C(20)-Si(1)-C(26)-C(27)	-5.06(16)
C(2)-Si(1)-C(26)-C(27)	116.93(13)
C(23)-Si(1)-C(26)-C(31)	51.62(14)
C(20)-Si(1)-C(26)-C(31)	170.16(12)
C(2)-Si(1)-C(26)-C(31)	-67.85(14)
C(31)-C(26)-C(27)-C(28)	-0.7(2)
Si(1)-C(26)-C(27)-C(28)	174.69(13)
C(26)-C(27)-C(28)-C(29)	0.2(3)
C(27)-C(28)-C(29)-C(30)	0.4(3)
C(28)-C(29)-C(30)-C(31)	-0.5(3)
C(29)-C(30)-C(31)-C(26)	0.0(3)
C(27)-C(26)-C(31)-C(30)	0.6(2)
Si(1)-C(26)-C(31)-C(30)	-174.93(13)

X-ray Data Collection, Structure Solution and Refinement for *N*-Toluenesulfonamide **S21**.

A colorless crystal of approximate dimensions 0.23 x 0.35 x 0.41 mm was mounted on a glass fiber and transferred to a Bruker CCD platform diffractometer. The SMART¹ program package was used to determine the unit-cell parameters and for data collection (25 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT² and SADABS³ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL⁴ program. The diffraction symmetry was *mmm* and the systematic absences were consistent with the orthorhombic space group *Pbca* which was later determined to be correct.

The structure was solved by direct methods and refined on F² by full-matrix least-squares techniques. The analytical scattering factors⁵ for neutral atoms were used throughout the analysis. Hydrogen atoms were located from a difference-Fourier map and refined (x,y,z and U_{iso}). At convergence, wR2 = 0.0986 and GOF = 1.101 for 416 variables refined against 6055 data (0.75 Å), R1 = 0.0370 for those 5075 data with I > 2.0σ(I).

References.

1. SMART Software Users Guide, Version 5.1, Bruker Analytical X-Ray Systems, Inc.; Madison, WI 1999.
2. SAINT Software Users Guide, Version 6.0, Bruker Analytical X-Ray Systems, Inc.; Madison, WI 1999.
3. Sheldrick, G. M. SADABS, Version 2.10, Bruker Analytical X-Ray Systems, Inc.; Madison, WI 2002.
4. Sheldrick, G. M. SHELXTL Version 6.12, Bruker Analytical X-Ray Systems, Inc.; Madison, WI 2001.
5. International Tables for X-Ray Crystallography 1992, Vol. C., Dordrecht: Kluwer Academic Publishers.

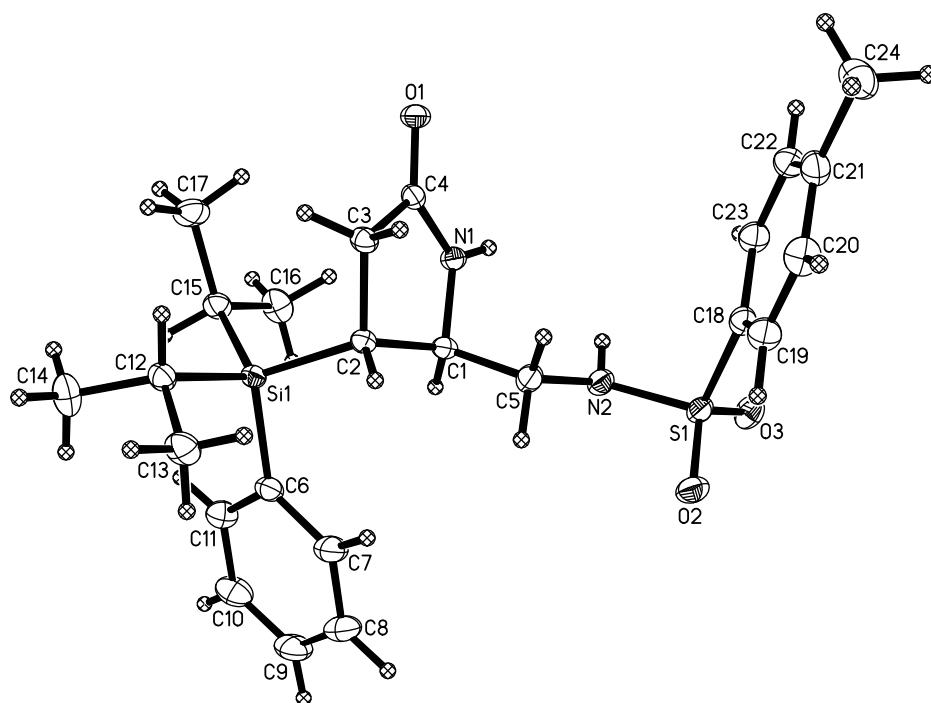
Definitions:

$$wR2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}$$

$$R1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$$

Goof = S = $[\Sigma[w(F_o^2 - F_c^2)^2] / (n-p)]^{1/2}$ where n is the number of reflections and p is the total number of parameters refined.

The thermal ellipsoid plot is shown at the 50% probability level.

Table 1. Crystal data and structure refinement for *N*-toluenesulfonamide **S21**.

Identification code	kaw91 (Nick Leonard)
Empirical formula	C ₂₄ H ₃₄ N ₂ O ₃ S Si
Formula weight	458.68
Temperature	163(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	<i>Pbca</i>
Unit cell dimensions	<i>a</i> = 16.431(3) Å $\square = 90^\circ$, <i>b</i> = 7.8966(13) Å $\square = 90^\circ$, <i>c</i> = 37.563(6) Å $\square = 90^\circ$.
Volume	4873.6(14) Å ³
<i>Z</i>	8
Density (calculated)	1.250 Mg/m ³
Absorption coefficient	0.209 mm ⁻¹
<i>F</i> (000)	1968
Crystal color	colorless
Crystal size	0.41 x 0.35 x 0.23 mm ³
Theta range for data collection	1.65 to 28.29°
Index ranges	-21 ≤ <i>h</i> ≤ 21, -10 ≤ <i>k</i> ≤ 10, -50 ≤ <i>l</i> ≤ 49
Reflections collected	50243
Independent reflections	6055 [R(int) = 0.0376]
Completeness to theta = 28.29°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9534 and 0.9190
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data / restraints / parameters	6055 / 0 / 416
Goodness-of-fit on <i>F</i> ²	1.101
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>) = 5075 data]	<i>R</i> 1 = 0.0370, <i>wR</i> 2 = 0.0914
<i>R</i> indices (all data, 0.75 Å)	<i>R</i> 1 = 0.0481, <i>wR</i> 2 = 0.0986

Largest diff. peak and hole 0.518 and -0.378 e.Å⁻³

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for *N*-toluenesulfonamide **S21**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(1)	5578(1)	7796(1)	2057(1)	18(1)
Si(1)	5177(1)	14046(1)	838(1)	15(1)
O(1)	7788(1)	12815(1)	1238(1)	21(1)
O(2)	4793(1)	8308(1)	2184(1)	24(1)
O(3)	5741(1)	6037(1)	1994(1)	24(1)
N(1)	6640(1)	11177(2)	1225(1)	16(1)
N(2)	5726(1)	8756(2)	1678(1)	18(1)
C(1)	5764(1)	11292(2)	1296(1)	16(1)
C(2)	5600(1)	13225(2)	1276(1)	15(1)
C(3)	6439(1)	13998(2)	1368(1)	17(1)
C(4)	7038(1)	12634(2)	1270(1)	16(1)
C(5)	5559(1)	10582(2)	1663(1)	19(1)
C(6)	4231(1)	12791(2)	734(1)	19(1)
C(7)	3762(1)	12024(2)	999(1)	27(1)
C(8)	3076(1)	11062(3)	919(1)	34(1)
C(9)	2837(1)	10853(2)	569(1)	32(1)
C(10)	3280(1)	11611(2)	300(1)	30(1)
C(11)	3967(1)	12563(2)	382(1)	24(1)
C(12)	4917(1)	16353(2)	912(1)	18(1)
C(13)	4268(1)	16570(2)	1202(1)	25(1)
C(14)	4646(1)	17248(2)	569(1)	30(1)
C(15)	5887(1)	13842(2)	442(1)	20(1)
C(16)	6112(1)	12019(2)	341(1)	27(1)
C(17)	6656(1)	14950(2)	464(1)	28(1)
C(18)	6321(1)	8573(2)	2354(1)	18(1)
C(19)	6084(1)	9511(2)	2649(1)	23(1)
C(20)	6681(1)	10098(2)	2881(1)	26(1)
C(21)	7502(1)	9782(2)	2819(1)	23(1)
C(22)	7726(1)	8862(2)	2517(1)	23(1)
C(23)	7141(1)	8254(2)	2285(1)	22(1)
C(24)	8143(1)	10423(3)	3071(1)	33(1)

Table 3. Bond lengths [\AA] and angles [$^\circ$] for *N*-toluenesulfonamide **S21**.

S(1)-O(2)	1.4336(11)
S(1)-O(3)	1.4346(12)
S(1)-N(2)	1.6335(13)
S(1)-C(18)	1.7639(15)
Si(1)-C(6)	1.8852(15)
Si(1)-C(12)	1.8919(15)
Si(1)-C(15)	1.8971(15)
Si(1)-C(2)	1.8987(15)
O(1)-C(4)	1.2455(17)
N(1)-C(4)	1.3342(18)
N(1)-C(1)	1.4669(17)
N(2)-C(5)	1.4688(19)
C(1)-C(5)	1.5257(19)
C(1)-C(2)	1.5515(19)
C(2)-C(3)	1.5460(19)
C(3)-C(4)	1.5053(19)

C(6)-C(7)	1.399(2)
C(6)-C(11)	1.403(2)
C(7)-C(8)	1.393(2)
C(8)-C(9)	1.382(3)
C(9)-C(10)	1.380(3)
C(10)-C(11)	1.391(2)
C(12)-C(13)	1.532(2)
C(12)-C(14)	1.536(2)
C(15)-C(16)	1.535(2)
C(15)-C(17)	1.540(2)
C(18)-C(19)	1.388(2)
C(18)-C(23)	1.395(2)
C(19)-C(20)	1.390(2)
C(20)-C(21)	1.392(2)
C(21)-C(22)	1.396(2)
C(21)-C(24)	1.503(2)
C(22)-C(23)	1.384(2)
O(2)-S(1)-O(3)	119.78(7)
O(2)-S(1)-N(2)	107.06(7)
O(3)-S(1)-N(2)	106.02(7)
O(2)-S(1)-C(18)	108.29(7)
O(3)-S(1)-C(18)	108.25(7)
N(2)-S(1)-C(18)	106.76(7)
C(6)-Si(1)-C(12)	110.51(6)
C(6)-Si(1)-C(15)	107.36(7)
C(12)-Si(1)-C(15)	109.63(7)
C(6)-Si(1)-C(2)	107.67(6)
C(12)-Si(1)-C(2)	106.49(6)
C(15)-Si(1)-C(2)	115.16(6)
C(4)-N(1)-C(1)	113.86(12)
C(5)-N(2)-S(1)	117.39(10)
N(1)-C(1)-C(5)	110.97(11)
N(1)-C(1)-C(2)	102.86(11)
C(5)-C(1)-C(2)	111.58(12)
C(3)-C(2)-C(1)	102.86(11)
C(3)-C(2)-Si(1)	112.66(10)
C(1)-C(2)-Si(1)	116.22(10)
C(4)-C(3)-C(2)	104.25(11)
O(1)-C(4)-N(1)	124.89(13)
O(1)-C(4)-C(3)	126.02(13)
N(1)-C(4)-C(3)	109.08(12)
N(2)-C(5)-C(1)	110.66(12)
C(7)-C(6)-C(11)	116.56(14)
C(7)-C(6)-Si(1)	122.18(12)
C(11)-C(6)-Si(1)	121.26(11)
C(8)-C(7)-C(6)	121.80(16)
C(9)-C(8)-C(7)	120.12(17)
C(10)-C(9)-C(8)	119.55(16)
C(9)-C(10)-C(11)	120.18(16)
C(10)-C(11)-C(6)	121.78(15)
C(13)-C(12)-C(14)	110.01(13)
C(13)-C(12)-Si(1)	111.68(11)
C(14)-C(12)-Si(1)	112.66(11)
C(16)-C(15)-C(17)	110.36(13)
C(16)-C(15)-Si(1)	114.98(11)
C(17)-C(15)-Si(1)	114.50(11)
C(19)-C(18)-C(23)	121.14(14)
C(19)-C(18)-S(1)	119.75(11)
C(23)-C(18)-S(1)	119.10(11)

C(18)-C(19)-C(20)	118.59(14)
C(19)-C(20)-C(21)	121.36(15)
C(20)-C(21)-C(22)	118.96(14)
C(20)-C(21)-C(24)	120.90(15)
C(22)-C(21)-C(24)	120.14(15)
C(23)-C(22)-C(21)	120.60(14)
C(22)-C(23)-C(18)	119.34(14)

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for *N*-toluenesulfonamide **S21**. The anisotropic displacement factor exponent takes the form: $-2 \square^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
S(1)	17(1)	16(1)	20(1)	2(1)	3(1)	-1(1)
Si(1)	12(1)	16(1)	16(1)	1(1)	0(1)	1(1)
O(1)	13(1)	16(1)	33(1)	1(1)	-2(1)	-1(1)
O(2)	17(1)	25(1)	29(1)	3(1)	6(1)	-1(1)
O(3)	29(1)	16(1)	28(1)	1(1)	5(1)	-1(1)
N(1)	13(1)	12(1)	23(1)	1(1)	1(1)	1(1)
N(2)	17(1)	18(1)	20(1)	2(1)	3(1)	0(1)
C(1)	12(1)	16(1)	20(1)	1(1)	-1(1)	-1(1)
C(2)	12(1)	16(1)	17(1)	1(1)	1(1)	1(1)
C(3)	15(1)	14(1)	22(1)	-1(1)	-3(1)	1(1)
C(4)	15(1)	15(1)	18(1)	1(1)	-3(1)	1(1)
C(5)	19(1)	17(1)	21(1)	2(1)	3(1)	0(1)
C(6)	14(1)	19(1)	23(1)	-1(1)	-1(1)	2(1)
C(7)	17(1)	36(1)	26(1)	4(1)	-2(1)	-4(1)
C(8)	19(1)	44(1)	39(1)	8(1)	-1(1)	-9(1)
C(9)	18(1)	32(1)	46(1)	-3(1)	-7(1)	-6(1)
C(10)	24(1)	34(1)	32(1)	-8(1)	-9(1)	-1(1)
C(11)	20(1)	27(1)	24(1)	-2(1)	-1(1)	-1(1)
C(12)	17(1)	18(1)	20(1)	0(1)	-1(1)	3(1)
C(13)	21(1)	26(1)	27(1)	-2(1)	4(1)	6(1)
C(14)	39(1)	25(1)	26(1)	4(1)	0(1)	11(1)
C(15)	16(1)	24(1)	18(1)	1(1)	3(1)	2(1)
C(16)	28(1)	29(1)	23(1)	-3(1)	3(1)	9(1)
C(17)	19(1)	39(1)	26(1)	2(1)	6(1)	-3(1)
C(18)	19(1)	17(1)	19(1)	2(1)	2(1)	1(1)
C(19)	20(1)	24(1)	24(1)	-1(1)	5(1)	5(1)
C(20)	29(1)	24(1)	23(1)	-4(1)	3(1)	3(1)
C(21)	25(1)	22(1)	24(1)	4(1)	-3(1)	0(1)
C(22)	18(1)	24(1)	28(1)	4(1)	2(1)	3(1)
C(23)	20(1)	23(1)	22(1)	1(1)	5(1)	3(1)
C(24)	32(1)	34(1)	31(1)	0(1)	-9(1)	1(1)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for *N*-toluenesulfonamide **S21**.

	x	y	z	U(eq)
H(1)	6877(12)	10190(30)	1194(5)	26(5)
H(2)	6150(13)	8490(30)	1590(5)	32(5)
H(1A)	5462(10)	10630(20)	1122(4)	14(4)
H(2A)	5213(11)	13500(20)	1461(5)	25(5)
H(3A)	6560(11)	15040(20)	1250(4)	19(4)
H(3B)	6486(12)	14190(20)	1619(5)	28(5)

H(5A)	4975(12)	10750(20)	1714(5)	25(5)
H(5B)	5869(11)	11220(20)	1844(5)	23(5)
H(7A)	3888(12)	12180(30)	1249(5)	32(5)
H(8A)	2757(13)	10500(30)	1109(6)	41(6)
H(9A)	2379(13)	10150(30)	514(5)	34(5)
H(10A)	3125(12)	11490(30)	72(5)	31(5)
H(11A)	4266(12)	13080(30)	188(5)	32(5)
H(12A)	5415(12)	16920(20)	1003(5)	27(5)
H(13A)	3769(14)	16010(30)	1136(6)	41(6)
H(13B)	4141(12)	17770(30)	1238(5)	31(5)
H(13C)	4443(12)	16090(30)	1427(5)	30(5)
H(14A)	5066(13)	17220(30)	399(6)	36(5)
H(14B)	4501(13)	18380(30)	618(5)	37(5)
H(14C)	4175(14)	16690(30)	461(6)	39(6)
H(15A)	5547(11)	14290(20)	241(5)	27(5)
H(16A)	5633(13)	11290(30)	317(5)	35(5)
H(16B)	6404(12)	11990(30)	116(6)	35(5)
H(16C)	6466(12)	11510(30)	522(5)	31(5)
H(17A)	6540(12)	16160(30)	525(5)	32(5)
H(17B)	6906(12)	15050(30)	231(6)	35(5)
H(17C)	7060(14)	14460(30)	618(6)	41(6)
H(19A)	5526(12)	9690(30)	2696(5)	29(5)
H(20A)	6518(12)	10760(30)	3080(5)	32(5)
H(22A)	8270(12)	8640(20)	2468(5)	29(5)
H(23A)	7278(11)	7610(20)	2083(5)	23(5)
H(24A)	8285(15)	9540(30)	3236(7)	54(7)
H(24B)	7909(15)	11350(40)	3209(7)	58(7)
H(24C)	8598(18)	10830(40)	2948(7)	71(9)

Table 6. Torsion angles [°] for *N*-toluenesulfonamide **S21**.

O(2)-S(1)-N(2)-C(5)	48.07(12)
O(3)-S(1)-N(2)-C(5)	177.02(11)
C(18)-S(1)-N(2)-C(5)	-67.72(12)
C(4)-N(1)-C(1)-C(5)	-101.27(14)
C(4)-N(1)-C(1)-C(2)	18.17(15)
N(1)-C(1)-C(2)-C(3)	-25.36(13)
C(5)-C(1)-C(2)-C(3)	93.65(13)
N(1)-C(1)-C(2)-Si(1)	98.21(11)
C(5)-C(1)-C(2)-Si(1)	-142.78(10)
C(6)-Si(1)-C(2)-C(3)	172.71(9)
C(12)-Si(1)-C(2)-C(3)	-68.74(11)
C(15)-Si(1)-C(2)-C(3)	53.00(12)
C(6)-Si(1)-C(2)-C(1)	54.39(11)
C(12)-Si(1)-C(2)-C(1)	172.94(10)
C(15)-Si(1)-C(2)-C(1)	-65.32(12)
C(1)-C(2)-C(3)-C(4)	24.49(14)
Si(1)-C(2)-C(3)-C(4)	-101.41(11)
C(1)-N(1)-C(4)-O(1)	176.95(13)
C(1)-N(1)-C(4)-C(3)	-2.31(16)
C(2)-C(3)-C(4)-O(1)	166.02(14)
C(2)-C(3)-C(4)-N(1)	-14.73(15)
S(1)-N(2)-C(5)-C(1)	177.43(9)
N(1)-C(1)-C(5)-N(2)	-65.41(15)
C(2)-C(1)-C(5)-N(2)	-179.47(11)
C(12)-Si(1)-C(6)-C(7)	-90.05(14)
C(15)-Si(1)-C(6)-C(7)	150.43(13)
C(2)-Si(1)-C(6)-C(7)	25.89(15)

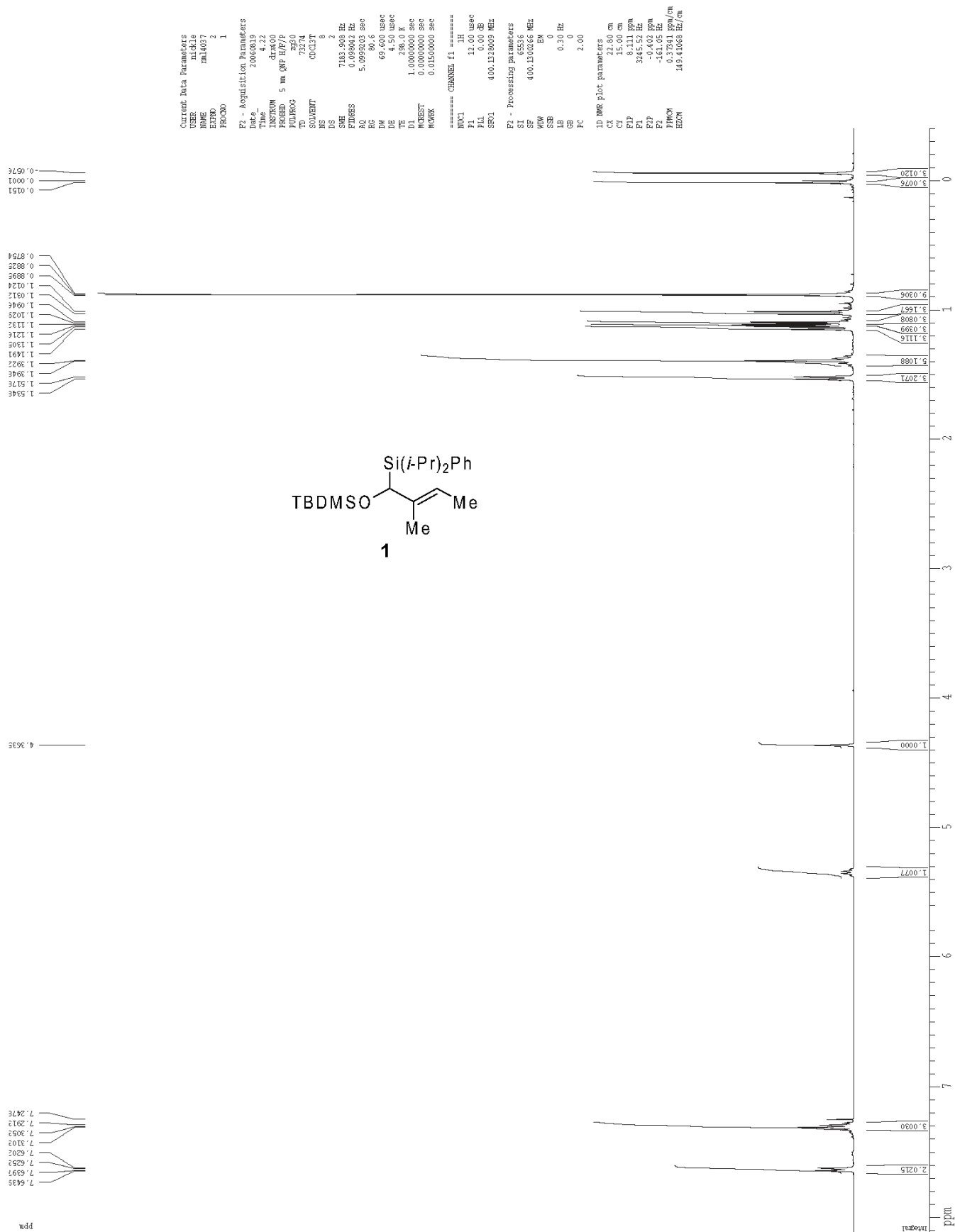
C(12)-Si(1)-C(6)-C(11)	90.78(13)
C(15)-Si(1)-C(6)-C(11)	-28.74(14)
C(2)-Si(1)-C(6)-C(11)	-153.29(12)
C(11)-C(6)-C(7)-C(8)	0.9(2)
Si(1)-C(6)-C(7)-C(8)	-178.26(14)
C(6)-C(7)-C(8)-C(9)	-0.5(3)
C(7)-C(8)-C(9)-C(10)	-0.3(3)
C(8)-C(9)-C(10)-C(11)	0.7(3)
C(9)-C(10)-C(11)-C(6)	-0.3(3)
C(7)-C(6)-C(11)-C(10)	-0.5(2)
Si(1)-C(6)-C(11)-C(10)	178.69(13)
C(6)-Si(1)-C(12)-C(13)	55.20(12)
C(15)-Si(1)-C(12)-C(13)	173.34(10)
C(2)-Si(1)-C(12)-C(13)	-61.46(12)
C(6)-Si(1)-C(12)-C(14)	-69.20(13)
C(15)-Si(1)-C(12)-C(14)	48.95(13)
C(2)-Si(1)-C(12)-C(14)	174.14(11)
C(6)-Si(1)-C(15)-C(16)	-56.97(13)
C(12)-Si(1)-C(15)-C(16)	-177.05(11)
C(2)-Si(1)-C(15)-C(16)	62.91(13)
C(6)-Si(1)-C(15)-C(17)	173.68(11)
C(12)-Si(1)-C(15)-C(17)	53.59(13)
C(2)-Si(1)-C(15)-C(17)	-66.44(13)
O(2)-S(1)-C(18)-C(19)	-0.27(14)
O(3)-S(1)-C(18)-C(19)	-131.55(12)
N(2)-S(1)-C(18)-C(19)	114.70(13)
O(2)-S(1)-C(18)-C(23)	-179.21(12)
O(3)-S(1)-C(18)-C(23)	49.51(14)
N(2)-S(1)-C(18)-C(23)	-64.24(13)
C(23)-C(18)-C(19)-C(20)	-1.5(2)
S(1)-C(18)-C(19)-C(20)	179.53(12)
C(18)-C(19)-C(20)-C(21)	0.9(2)
C(19)-C(20)-C(21)-C(22)	0.3(2)
C(19)-C(20)-C(21)-C(24)	179.98(16)
C(20)-C(21)-C(22)-C(23)	-0.9(2)
C(24)-C(21)-C(22)-C(23)	179.48(16)
C(21)-C(22)-C(23)-C(18)	0.2(2)
C(19)-C(18)-C(23)-C(22)	1.0(2)
S(1)-C(18)-C(23)-C(22)	179.96(12)

VIII. References

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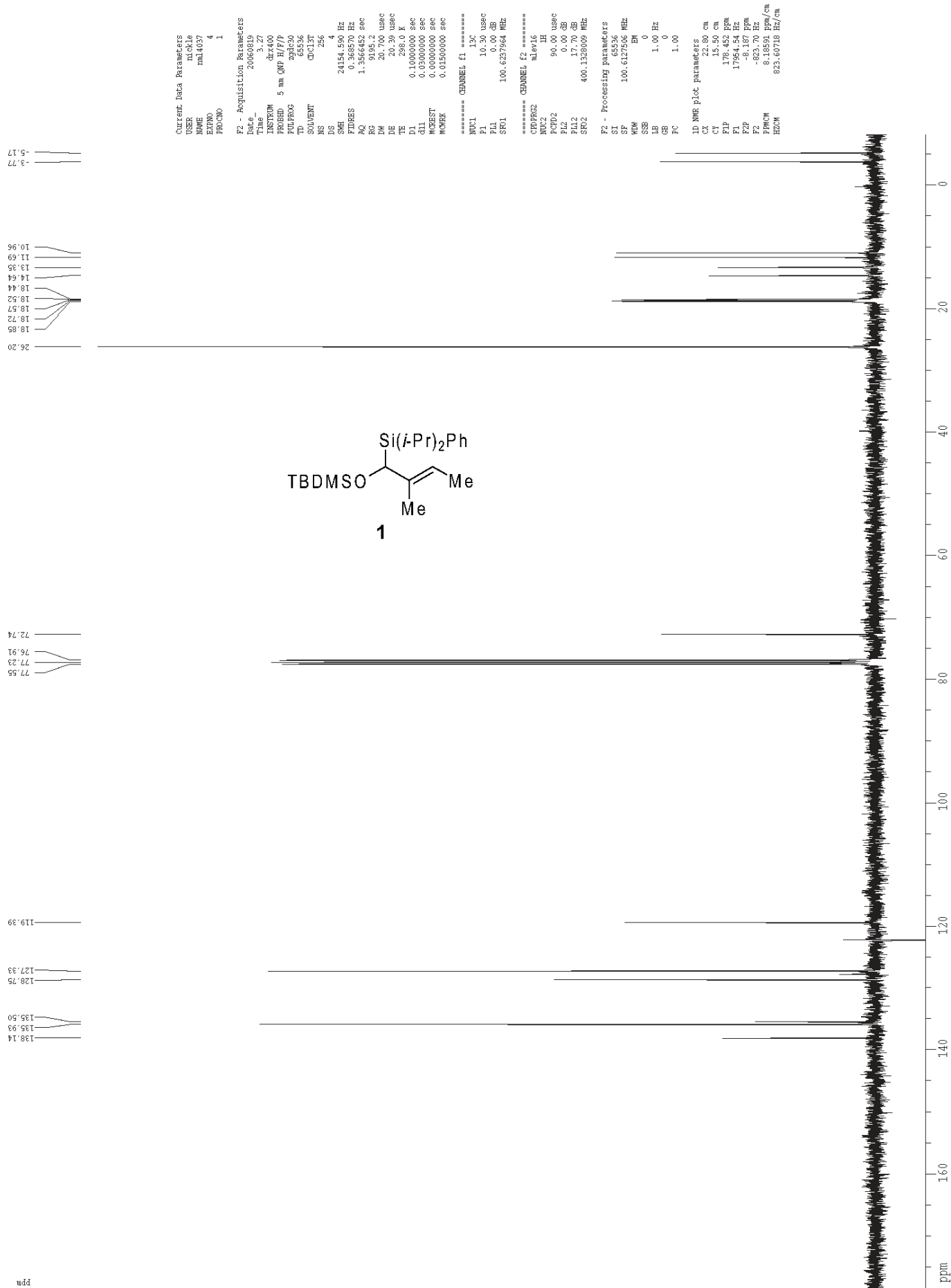
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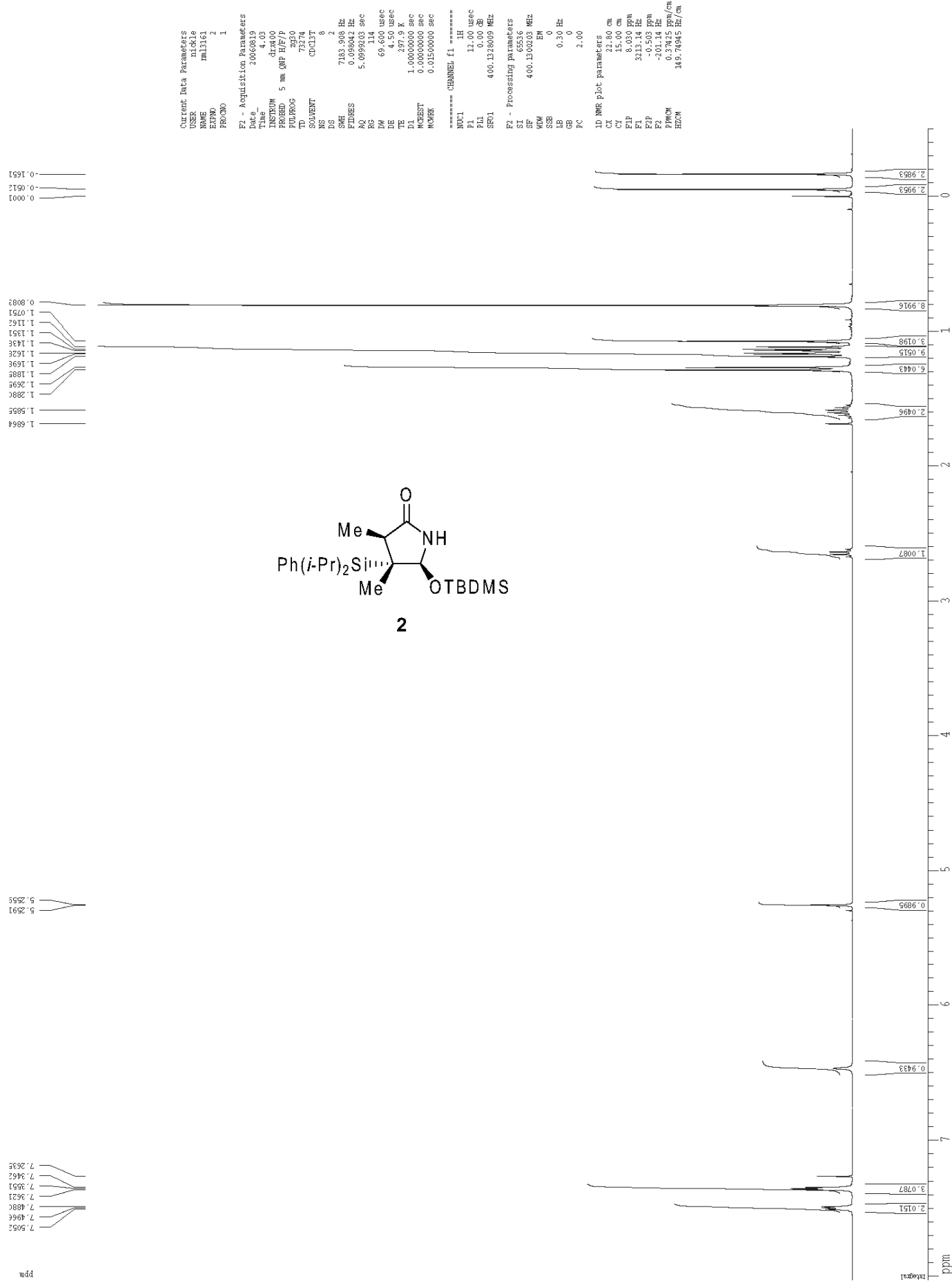


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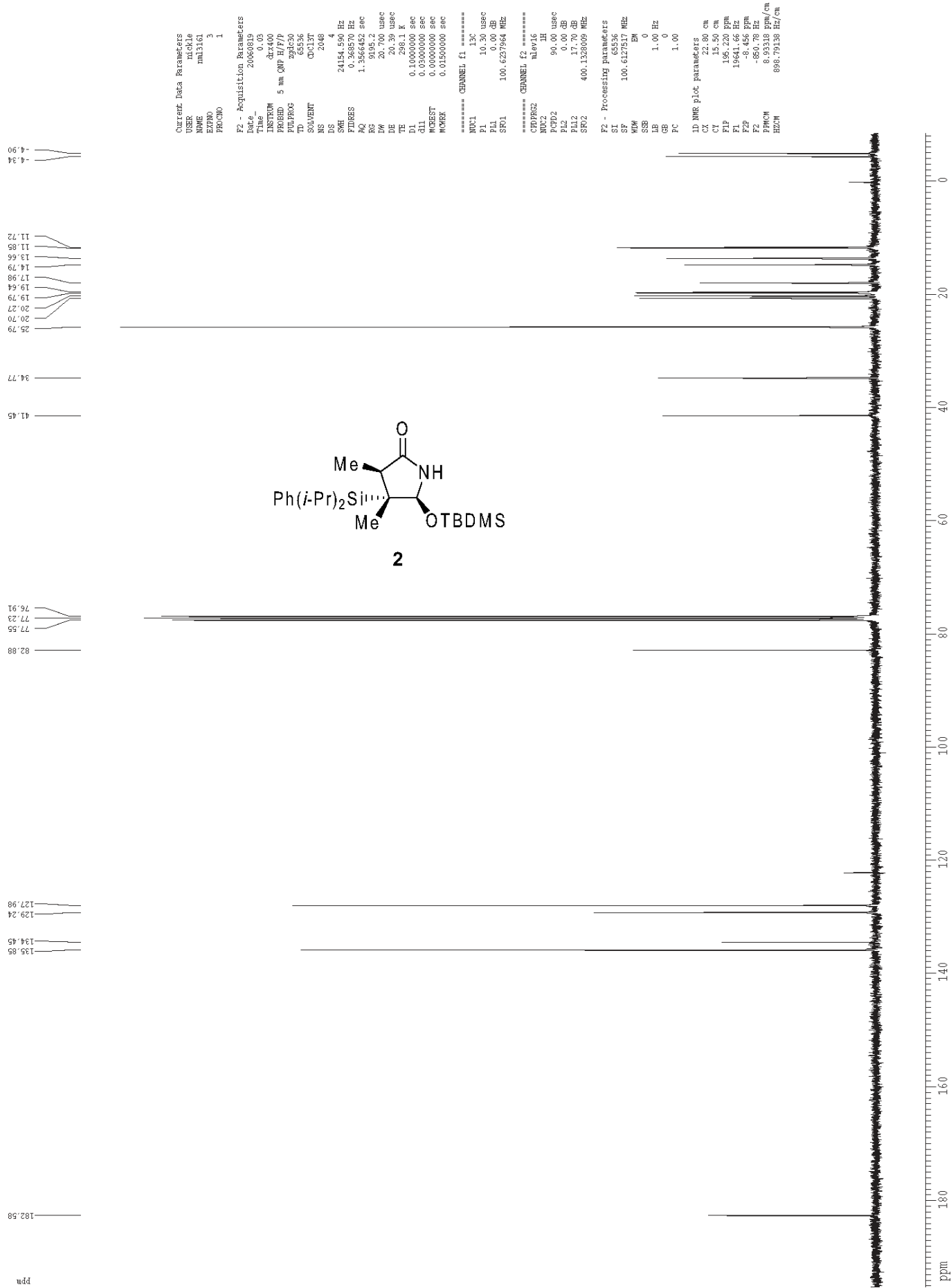
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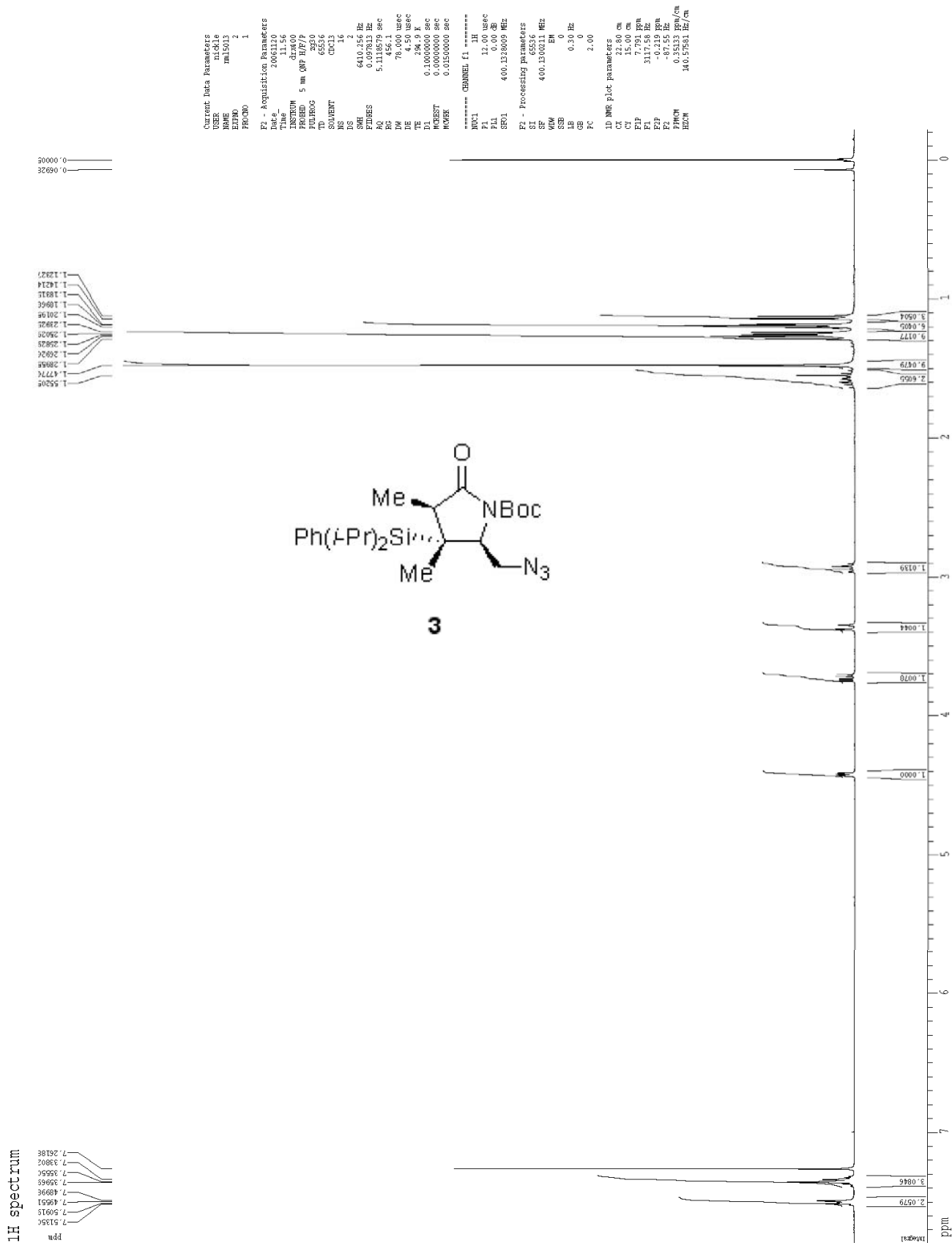


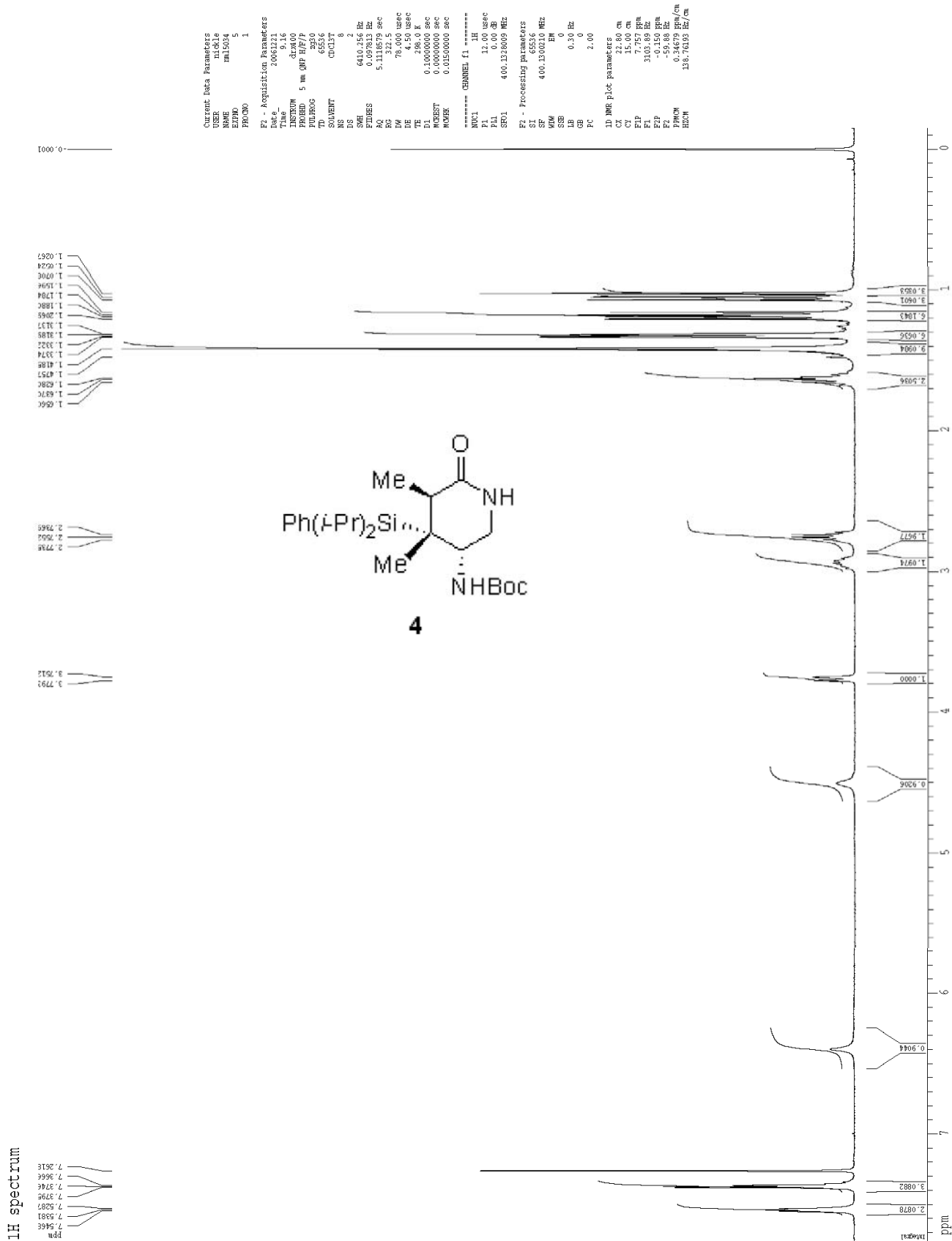
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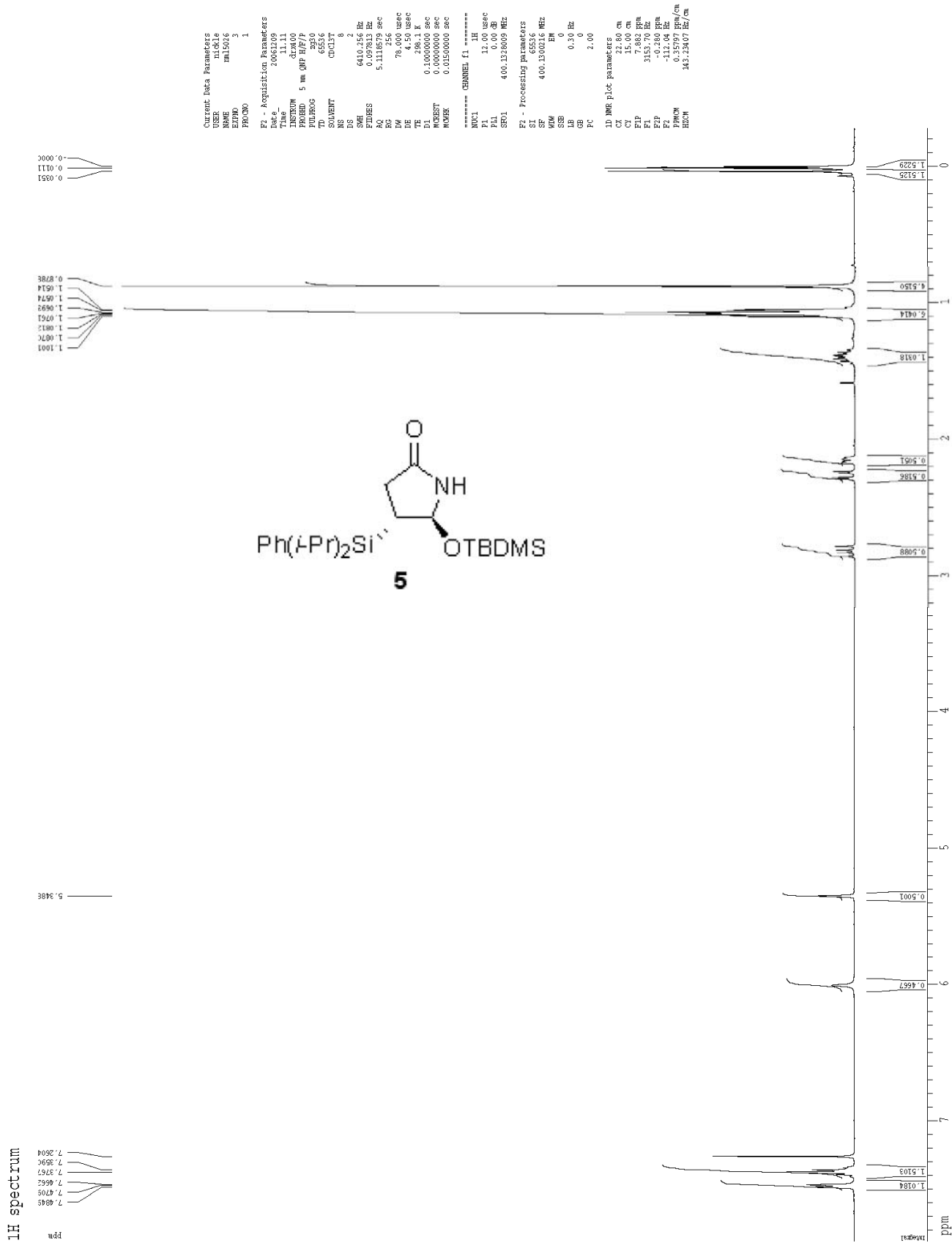


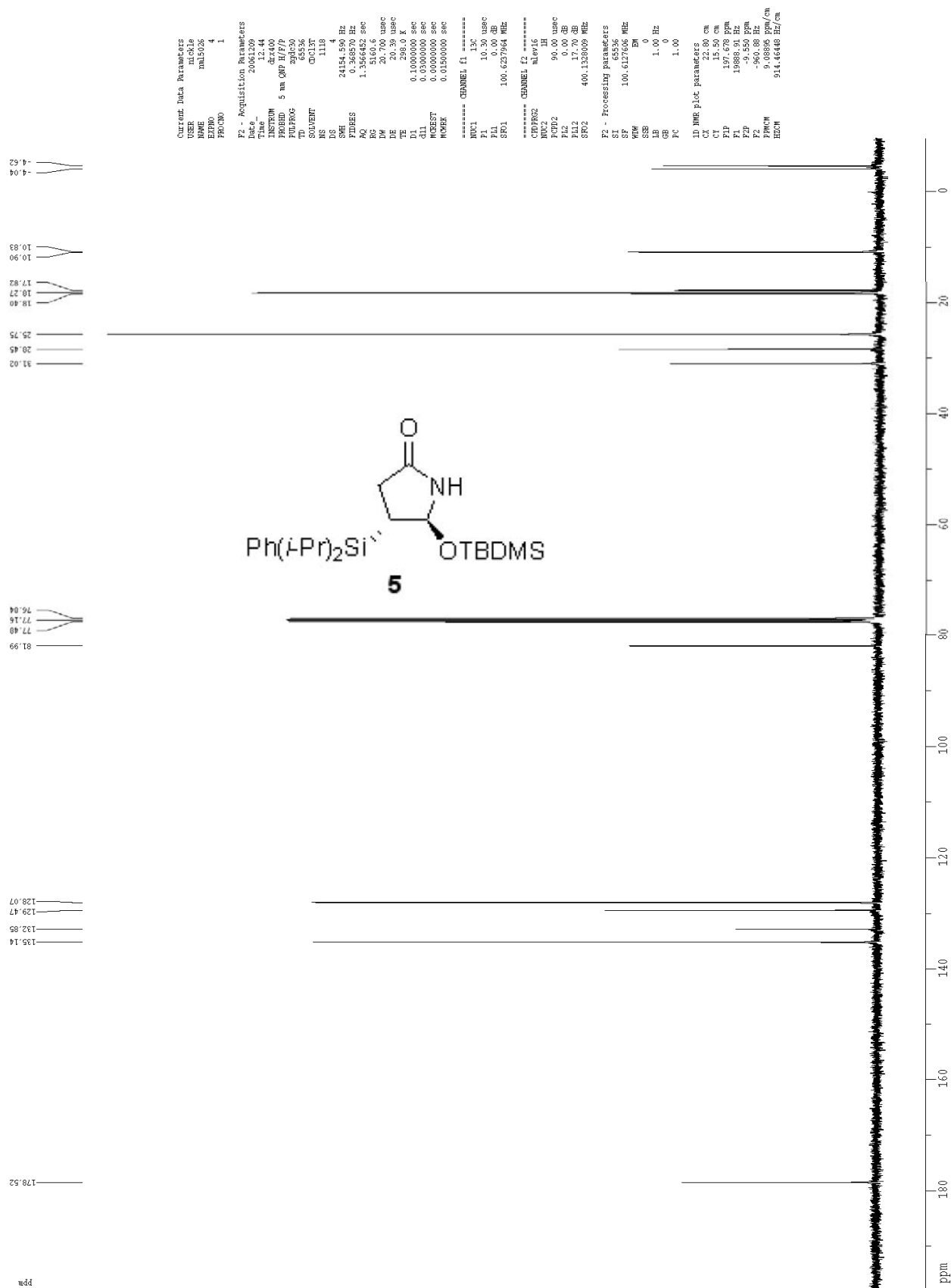
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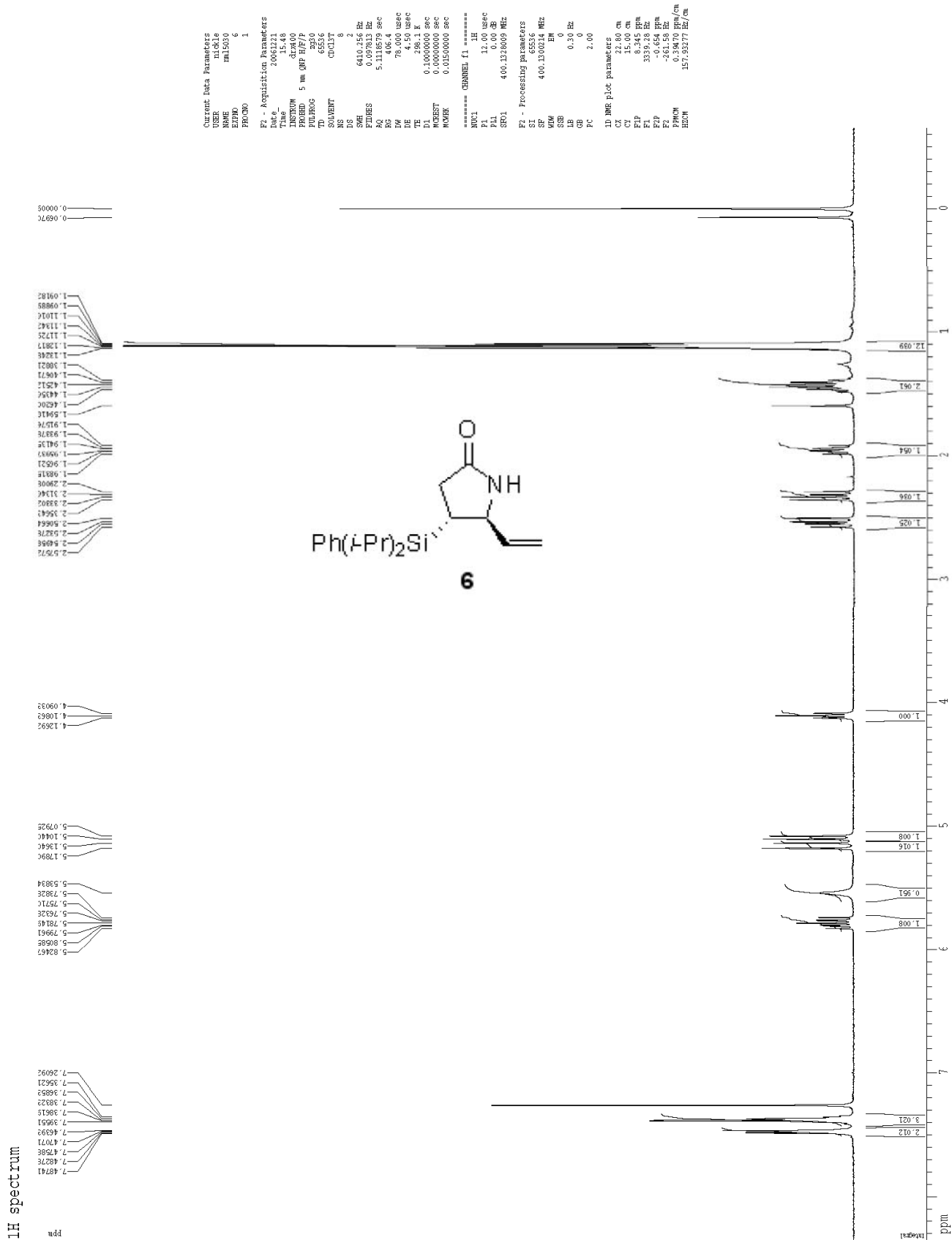


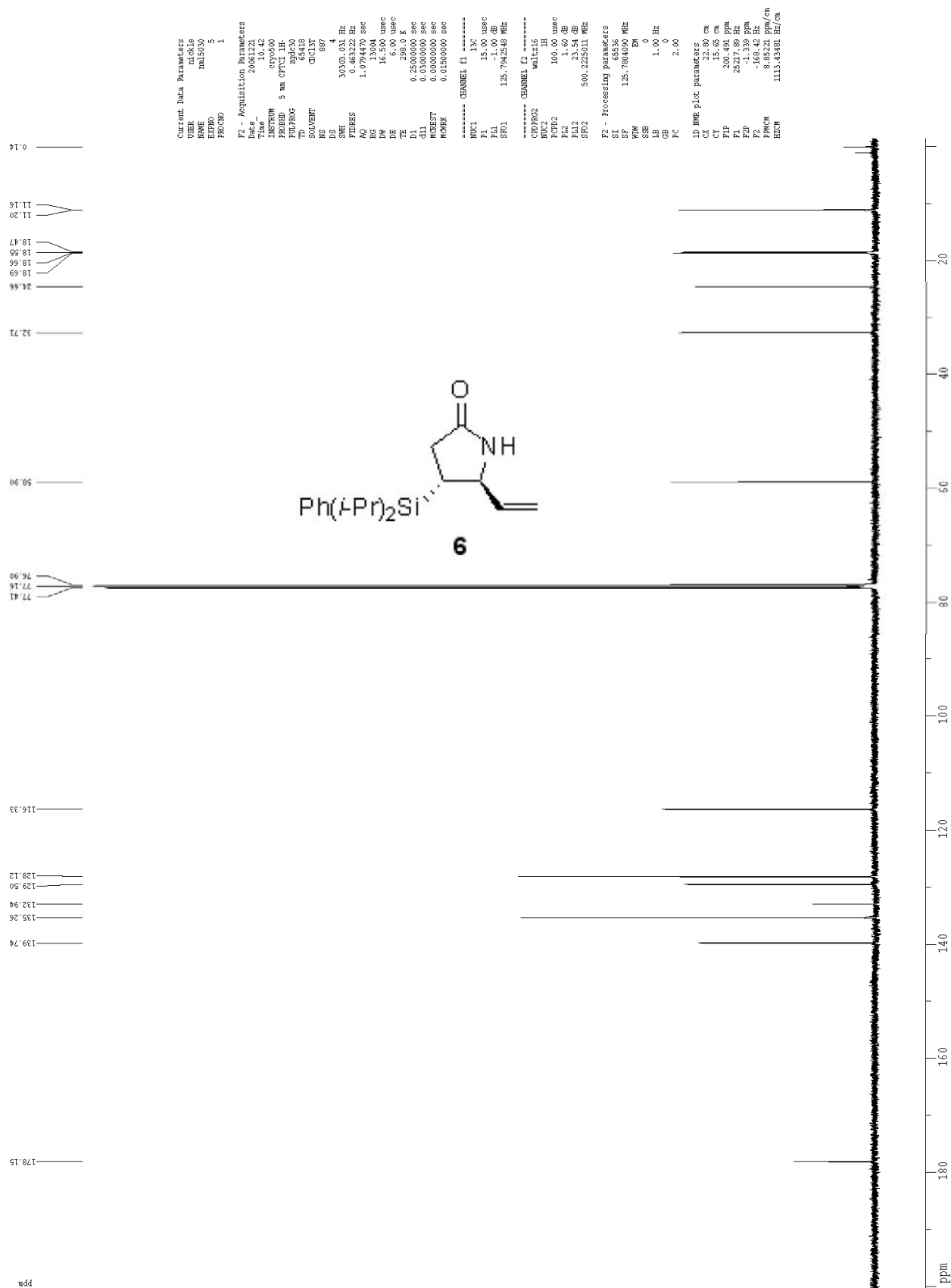


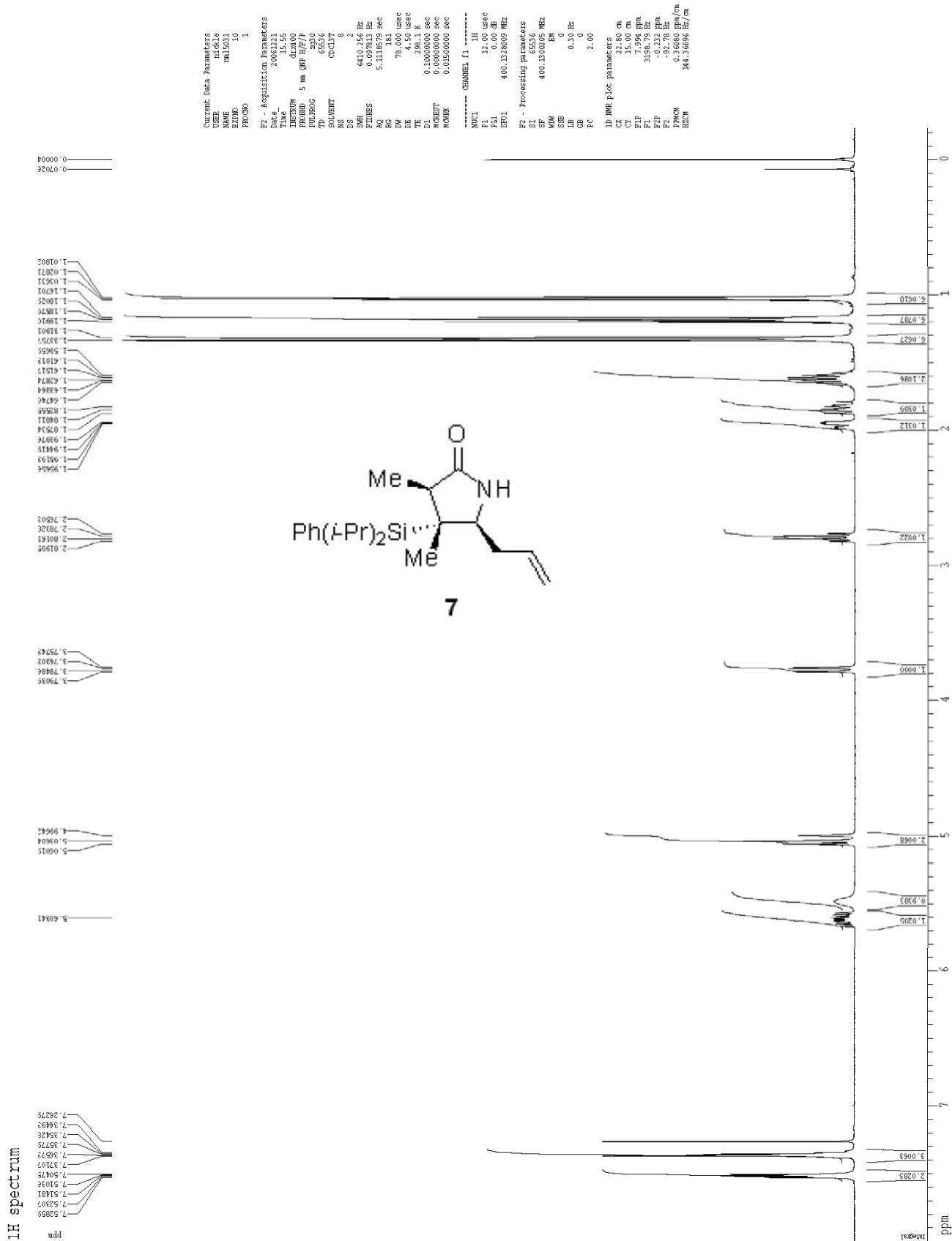


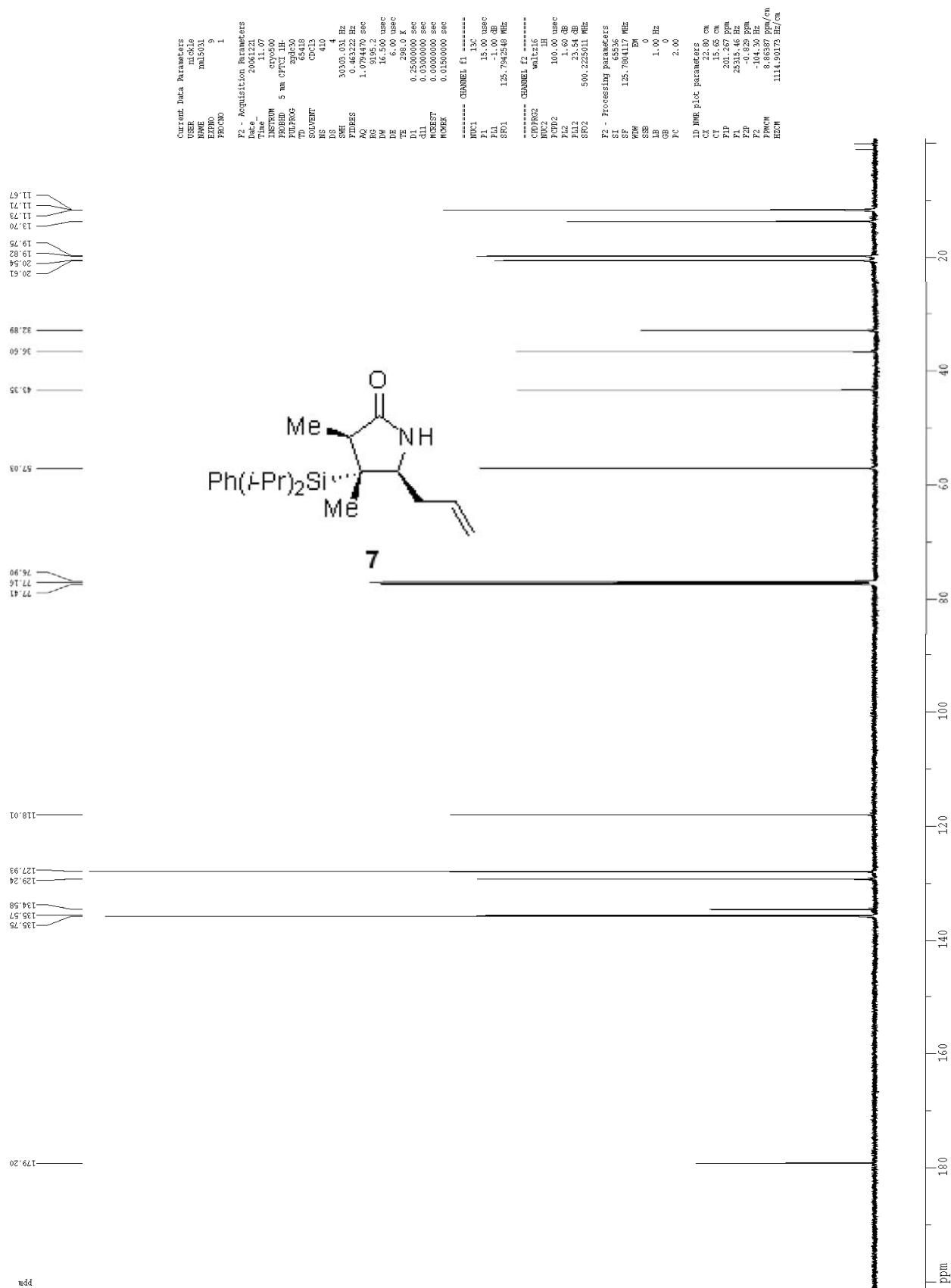


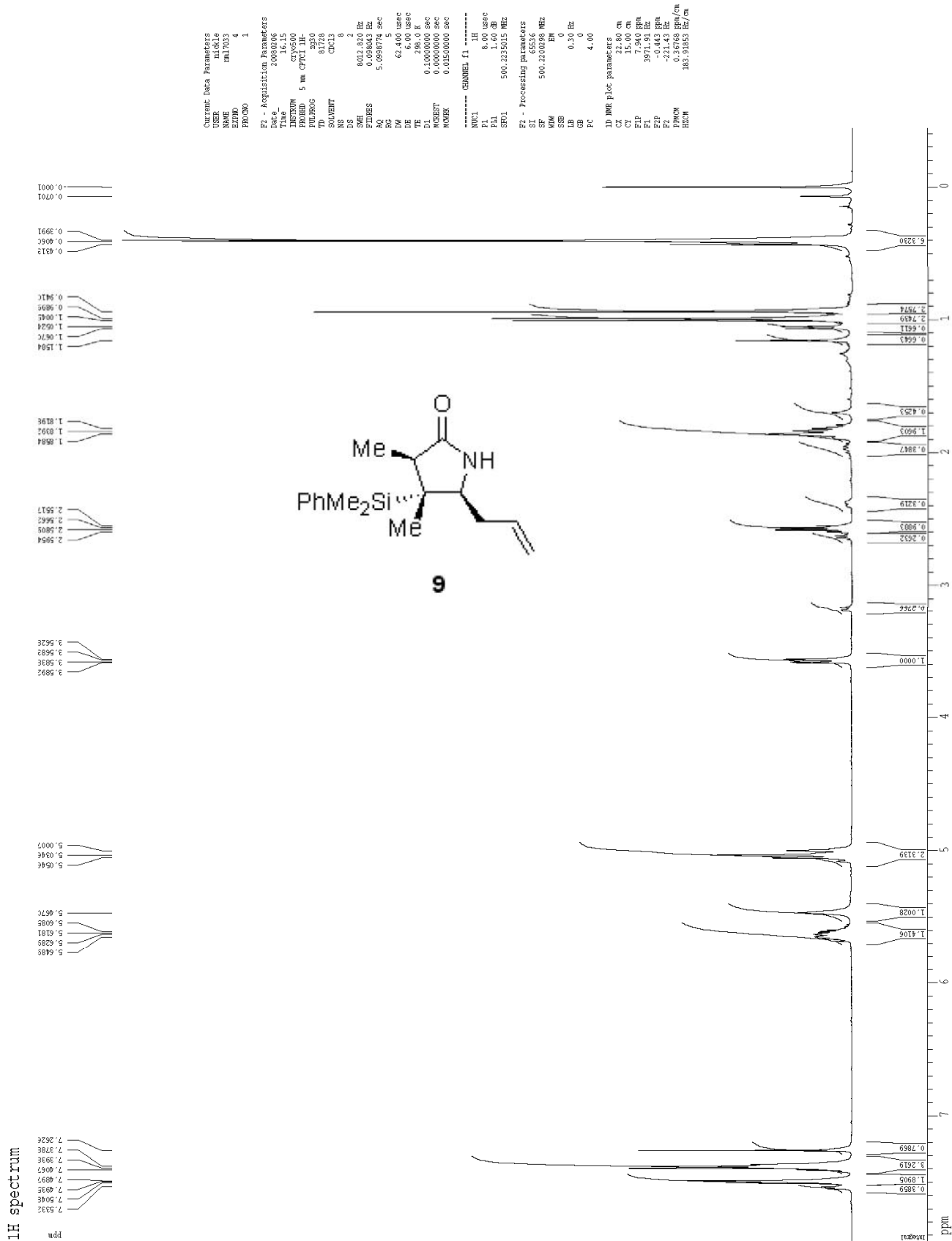
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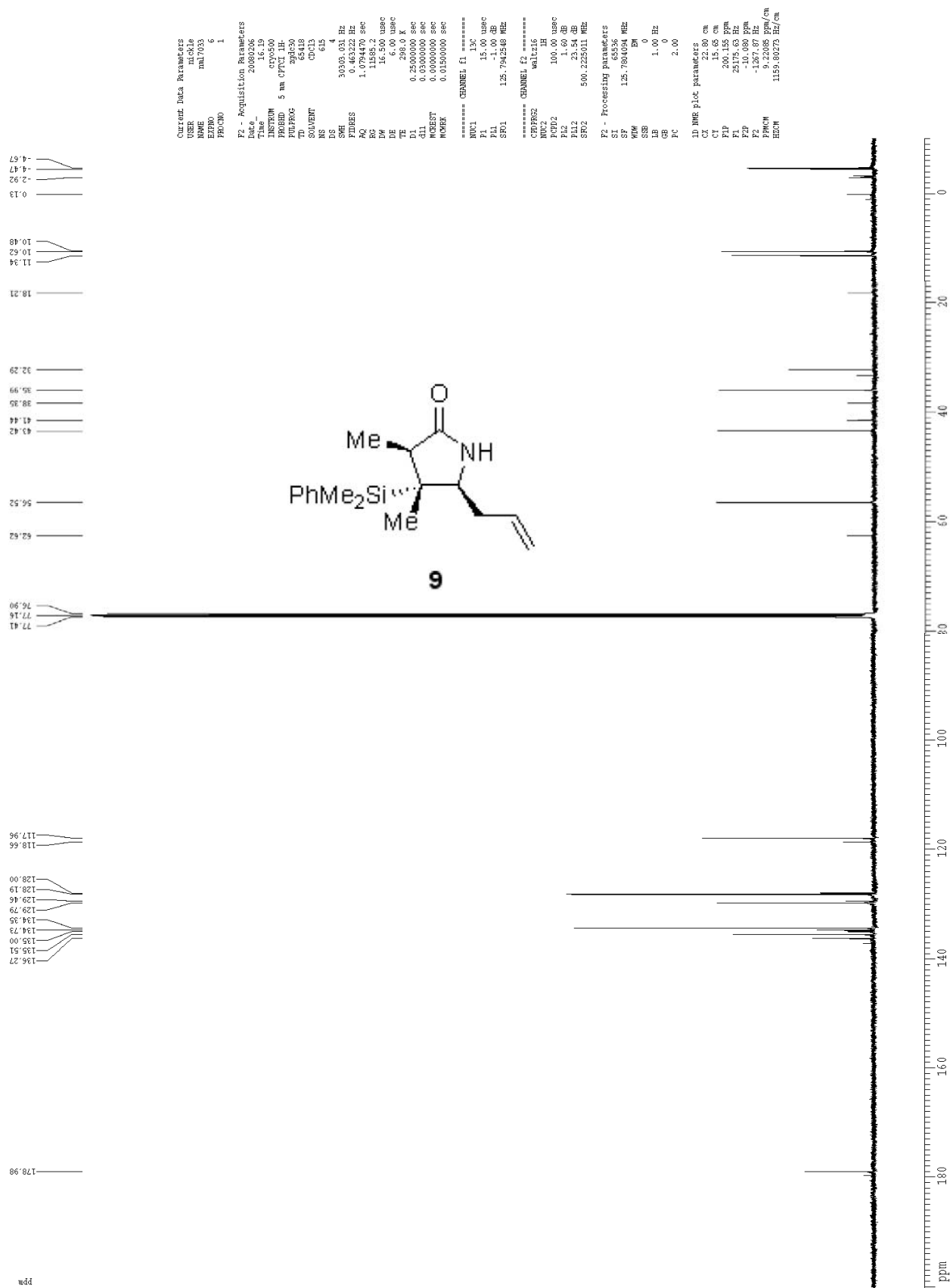


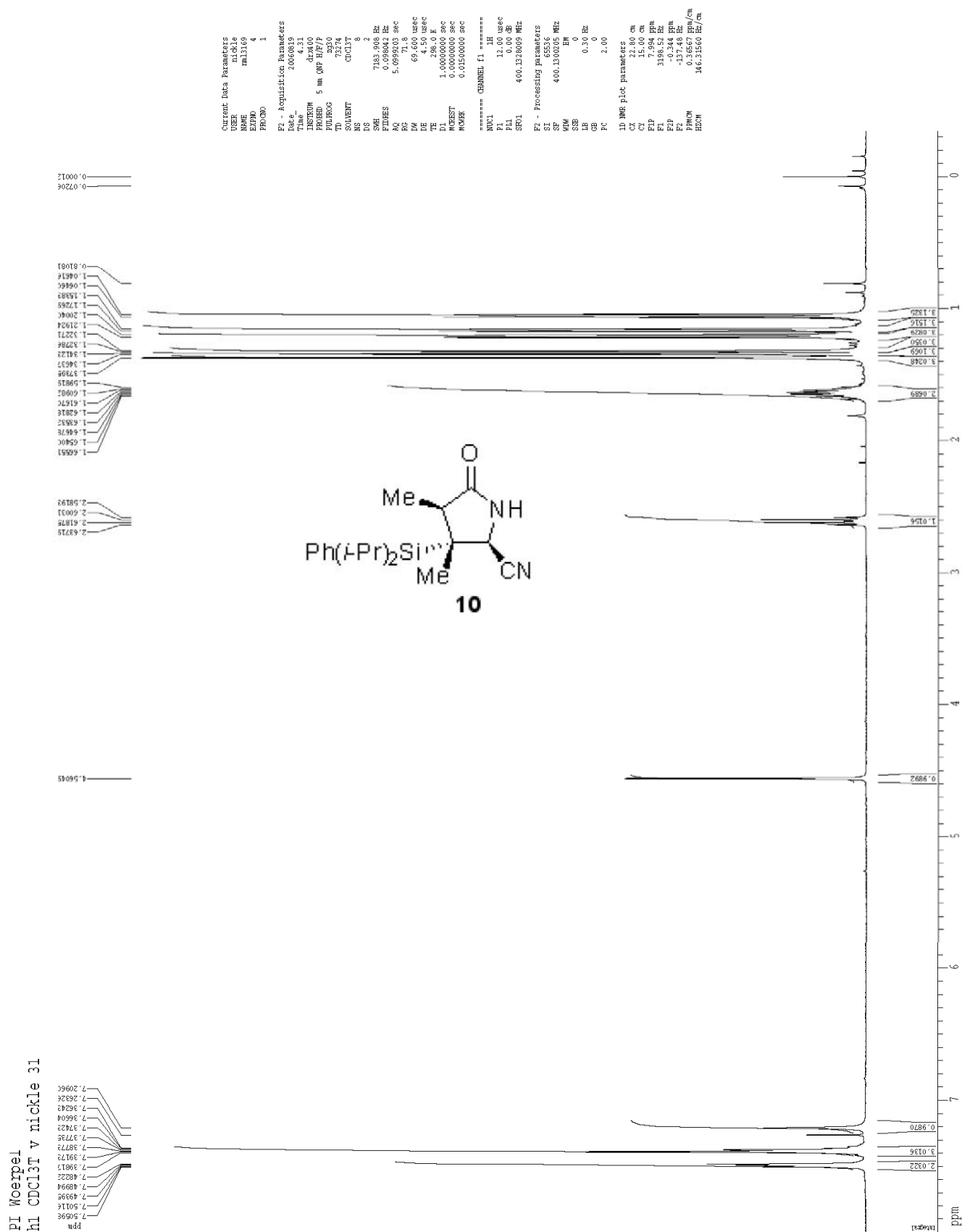
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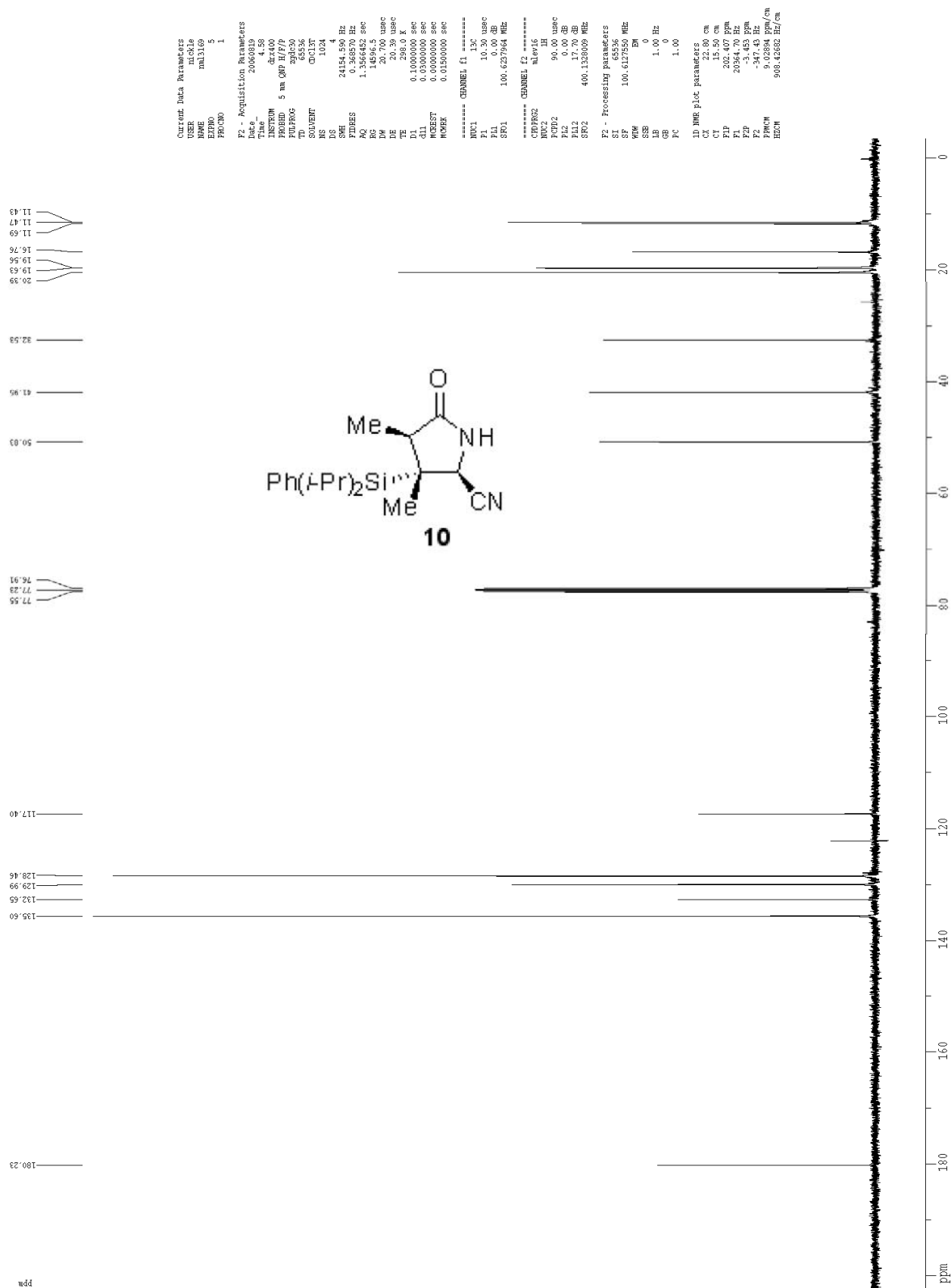
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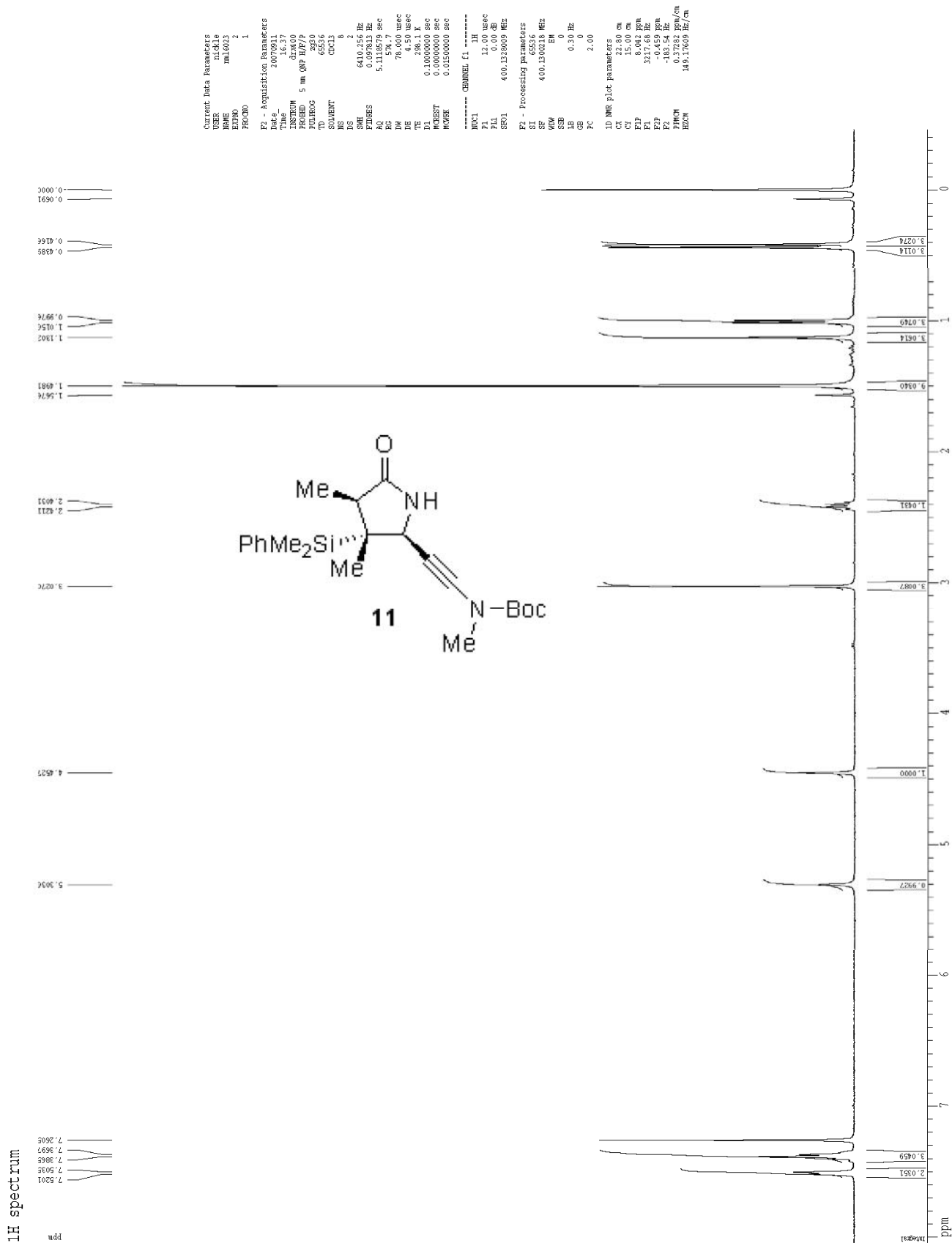


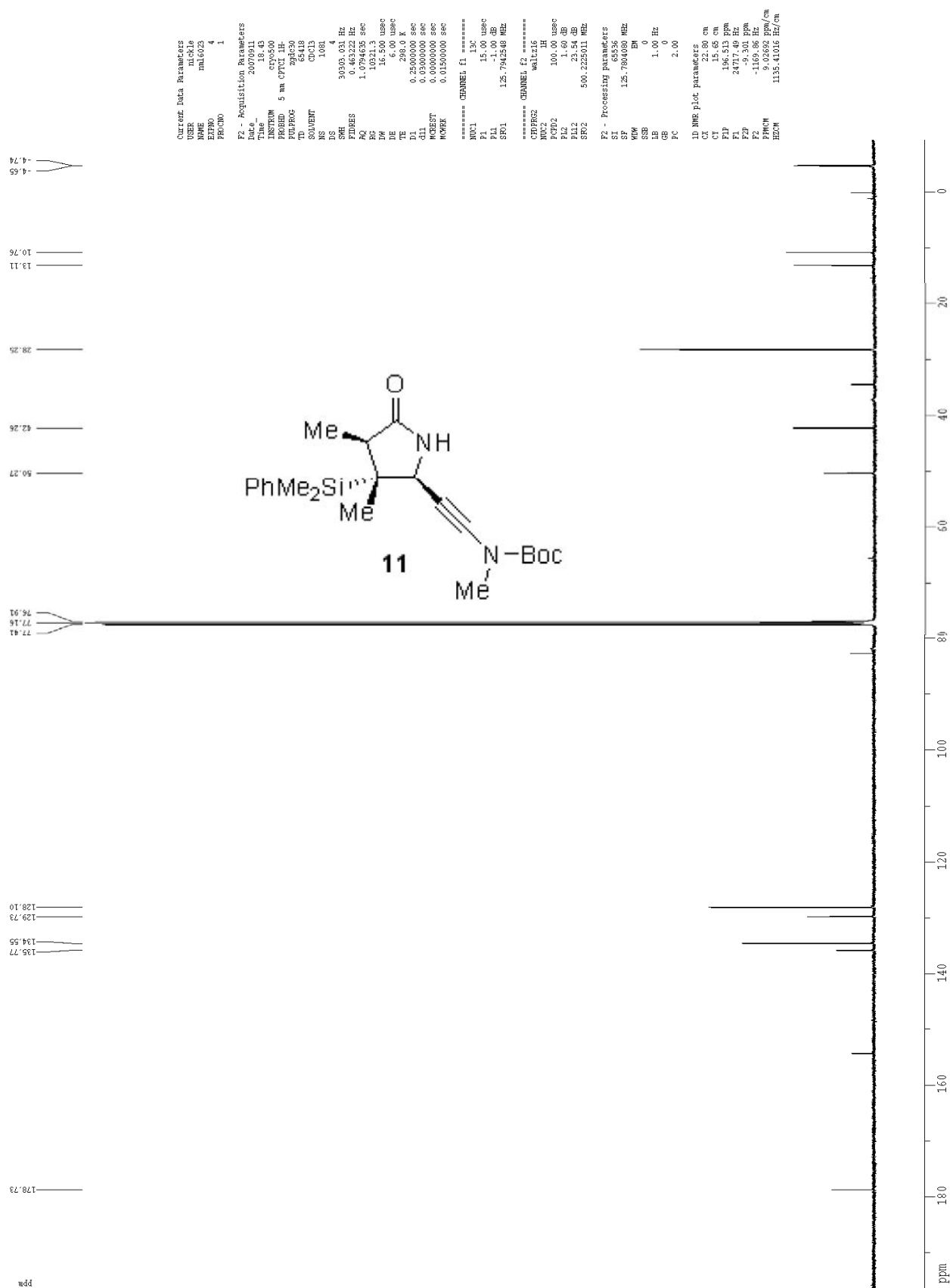
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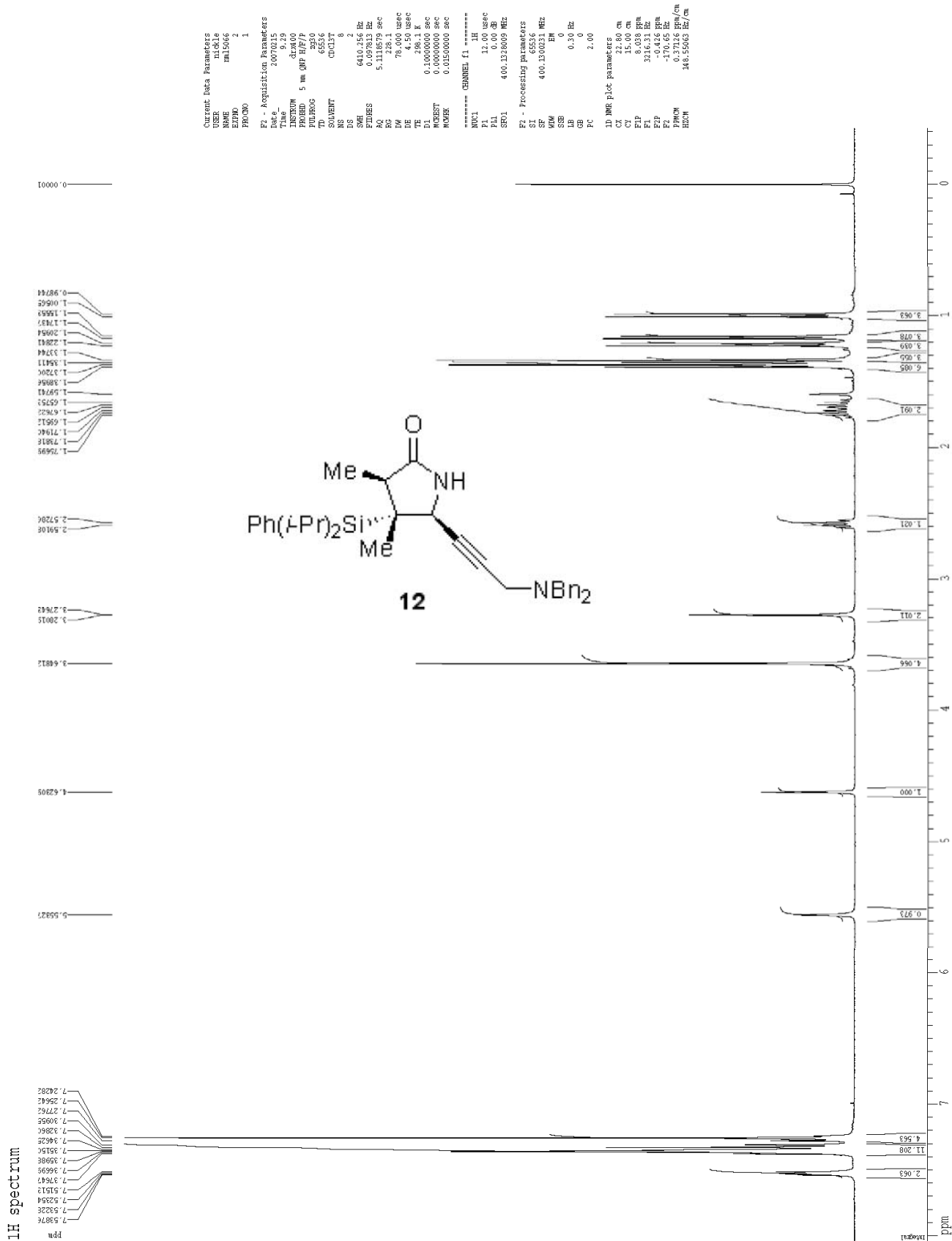


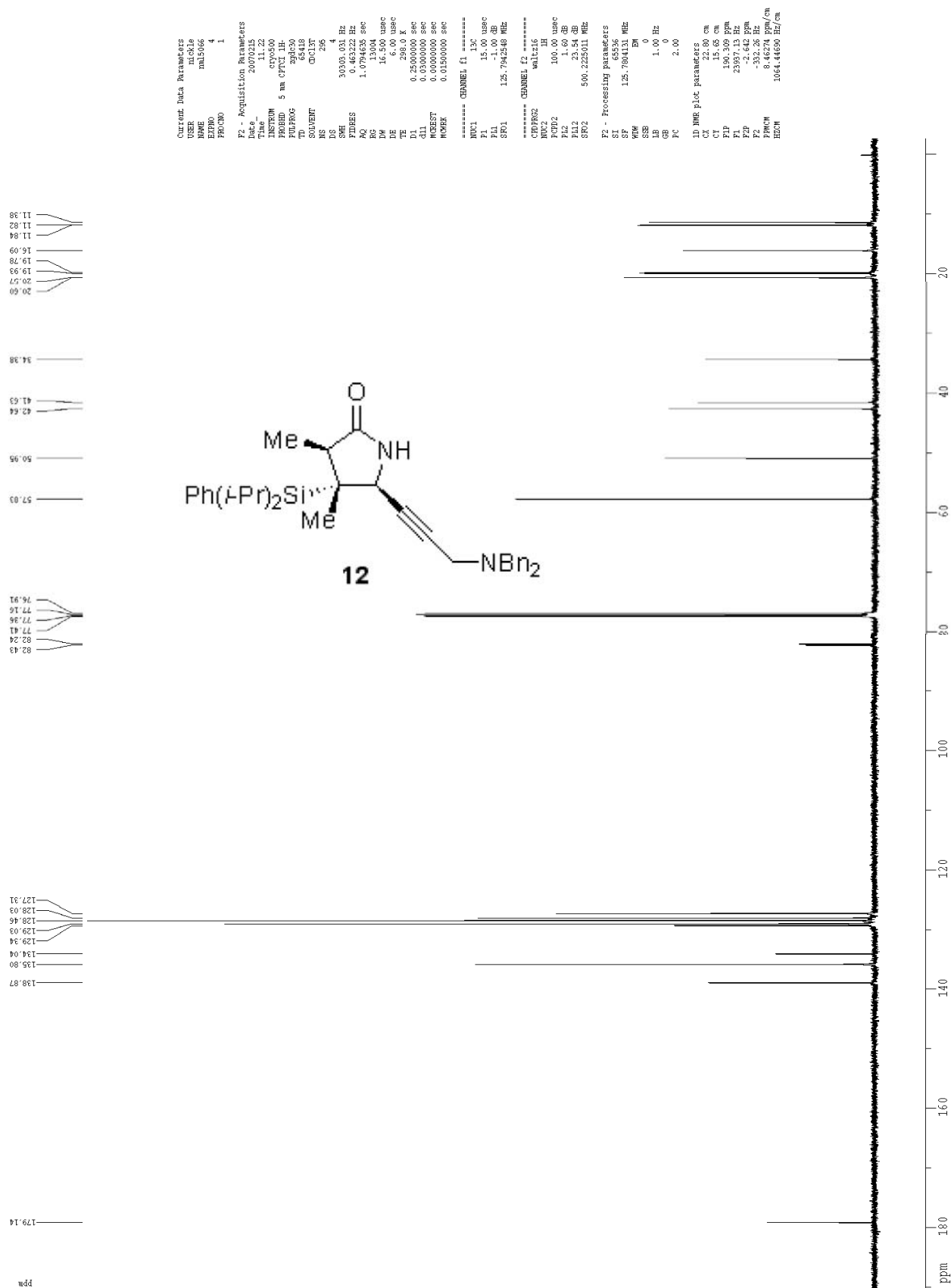
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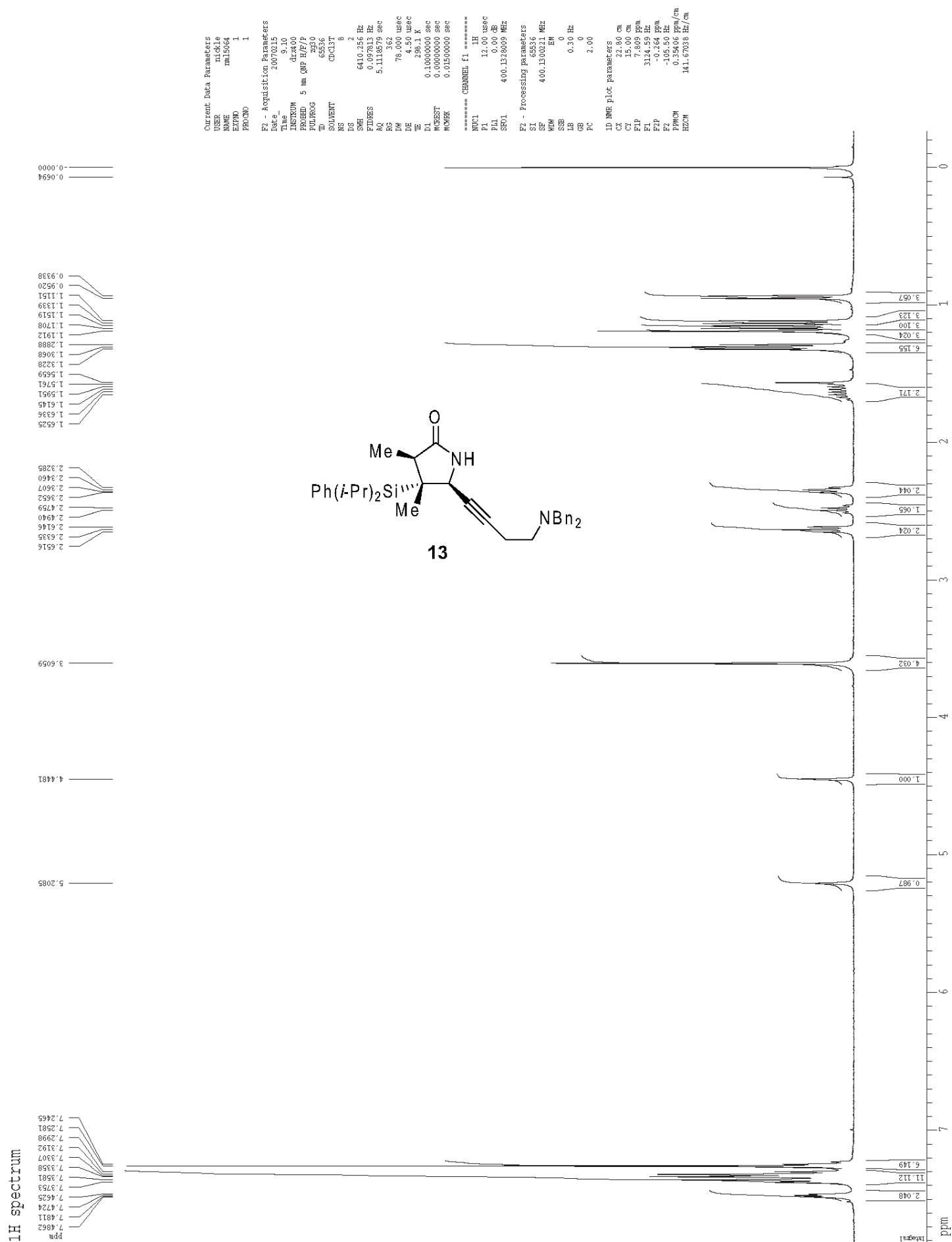


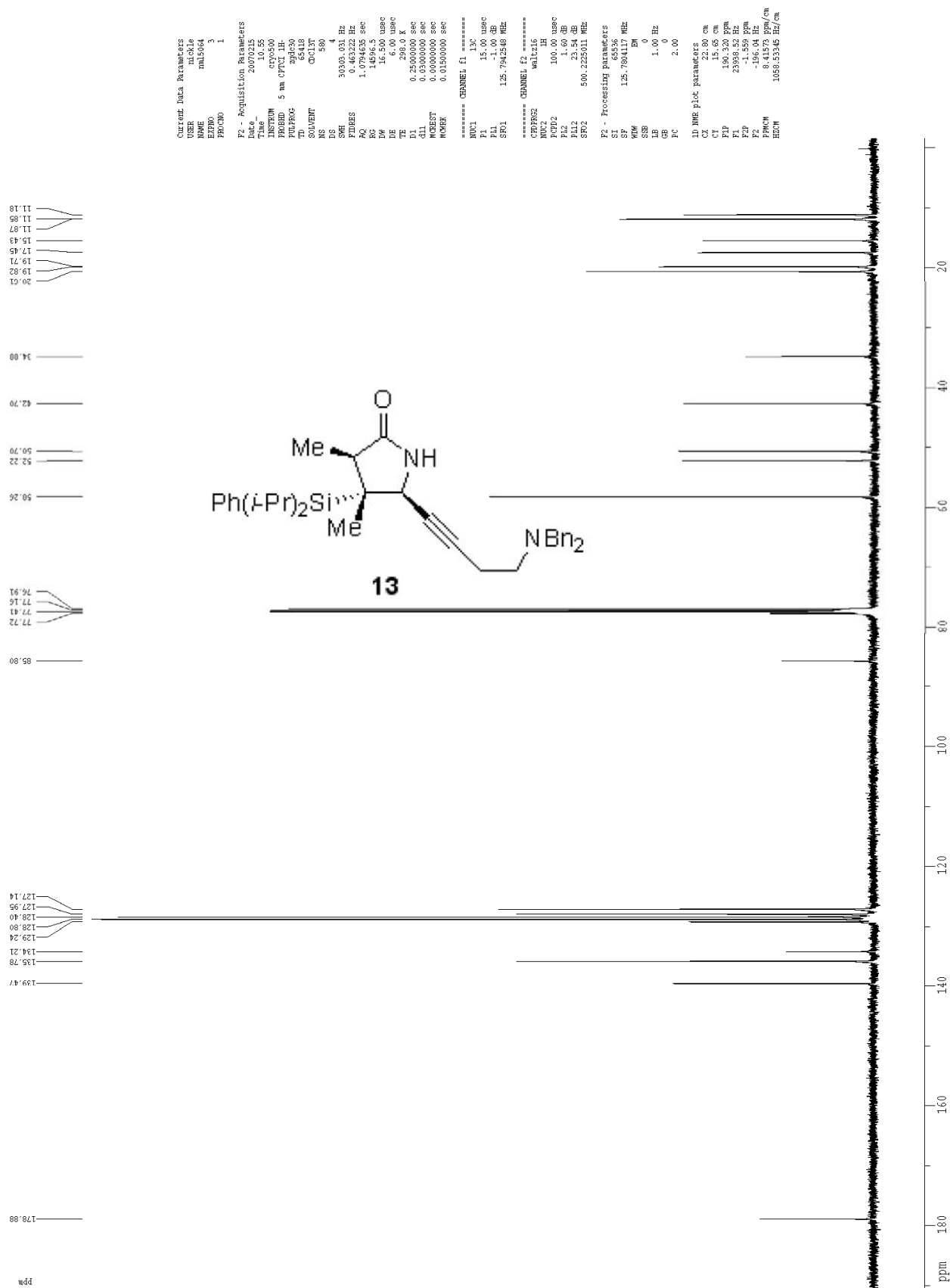


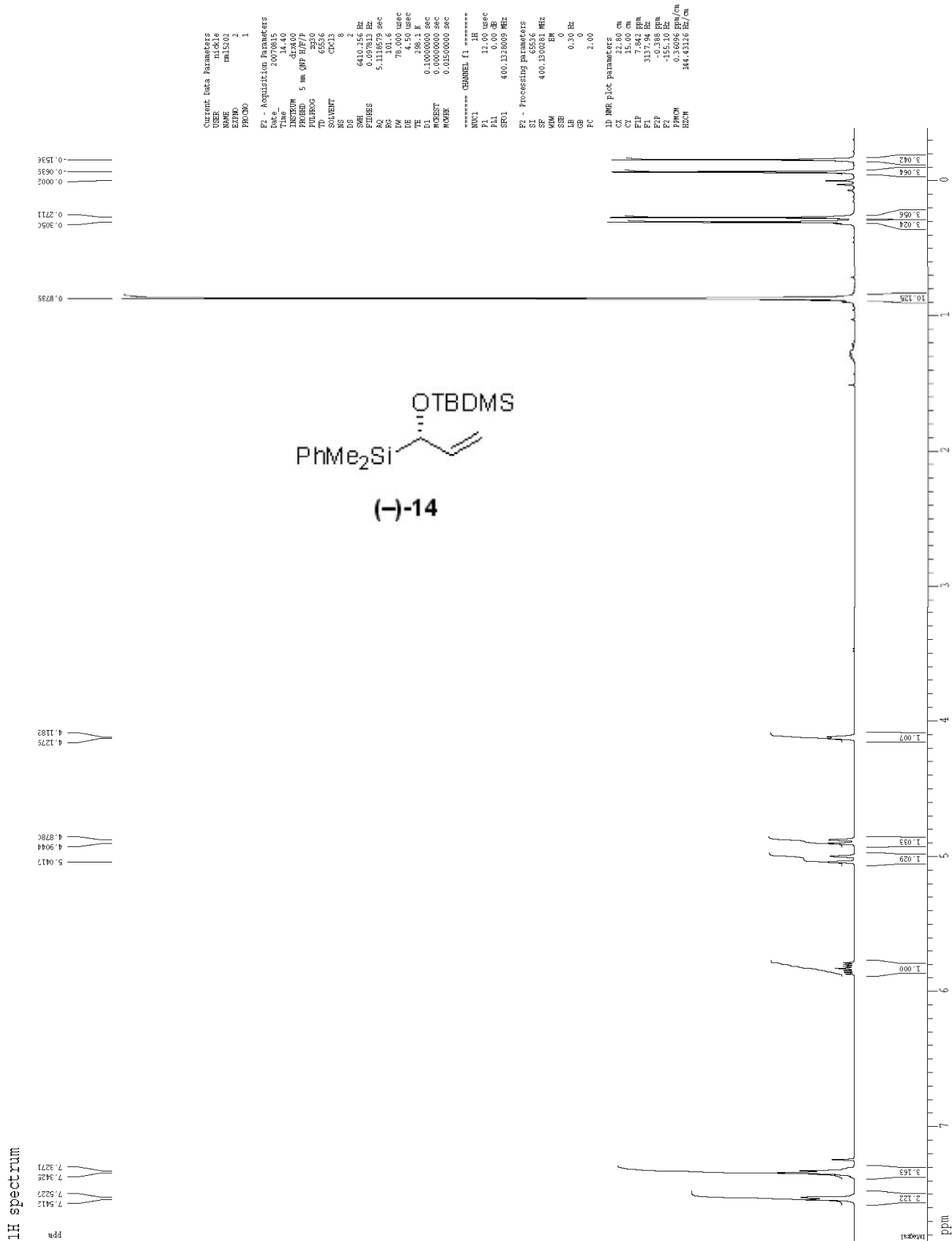
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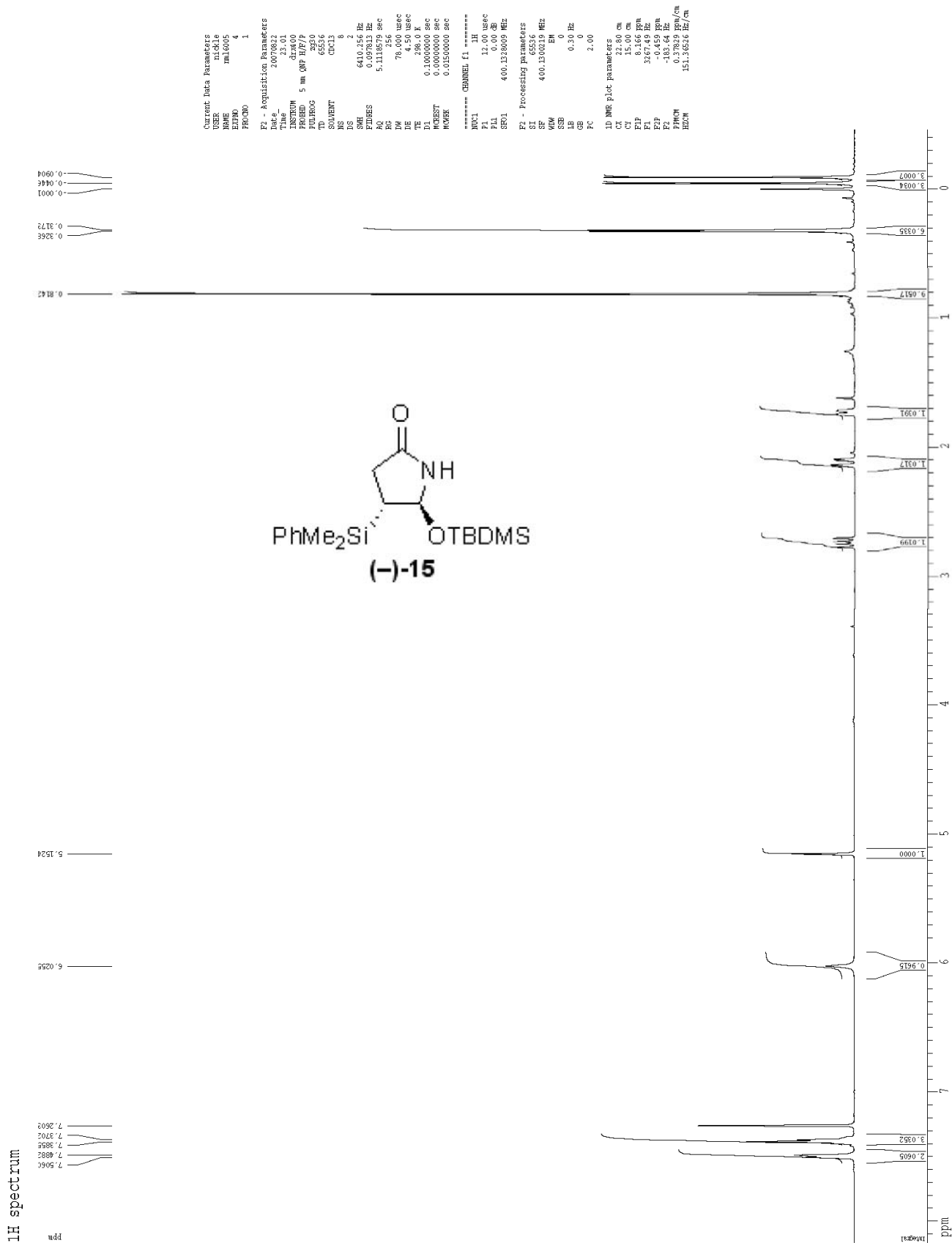


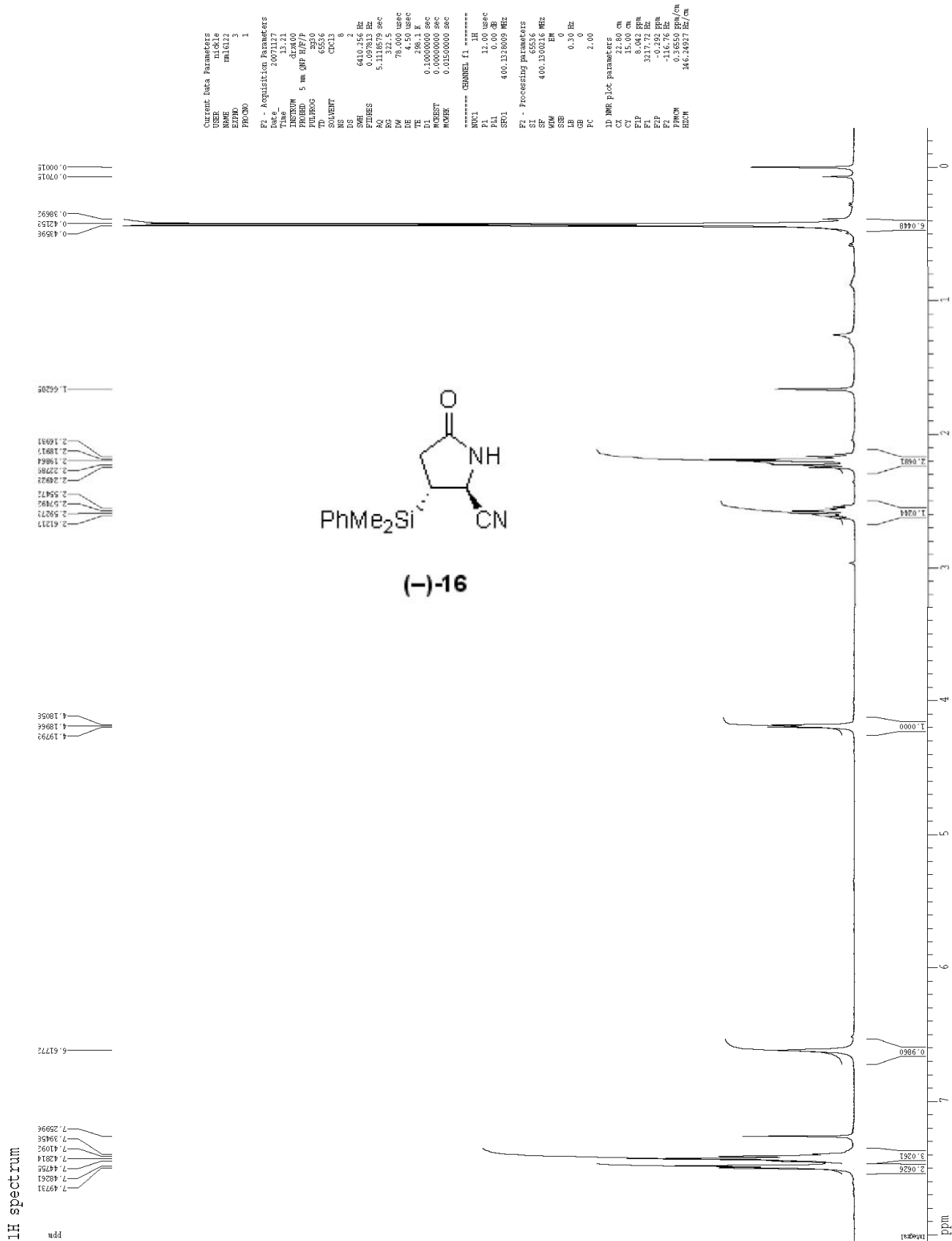
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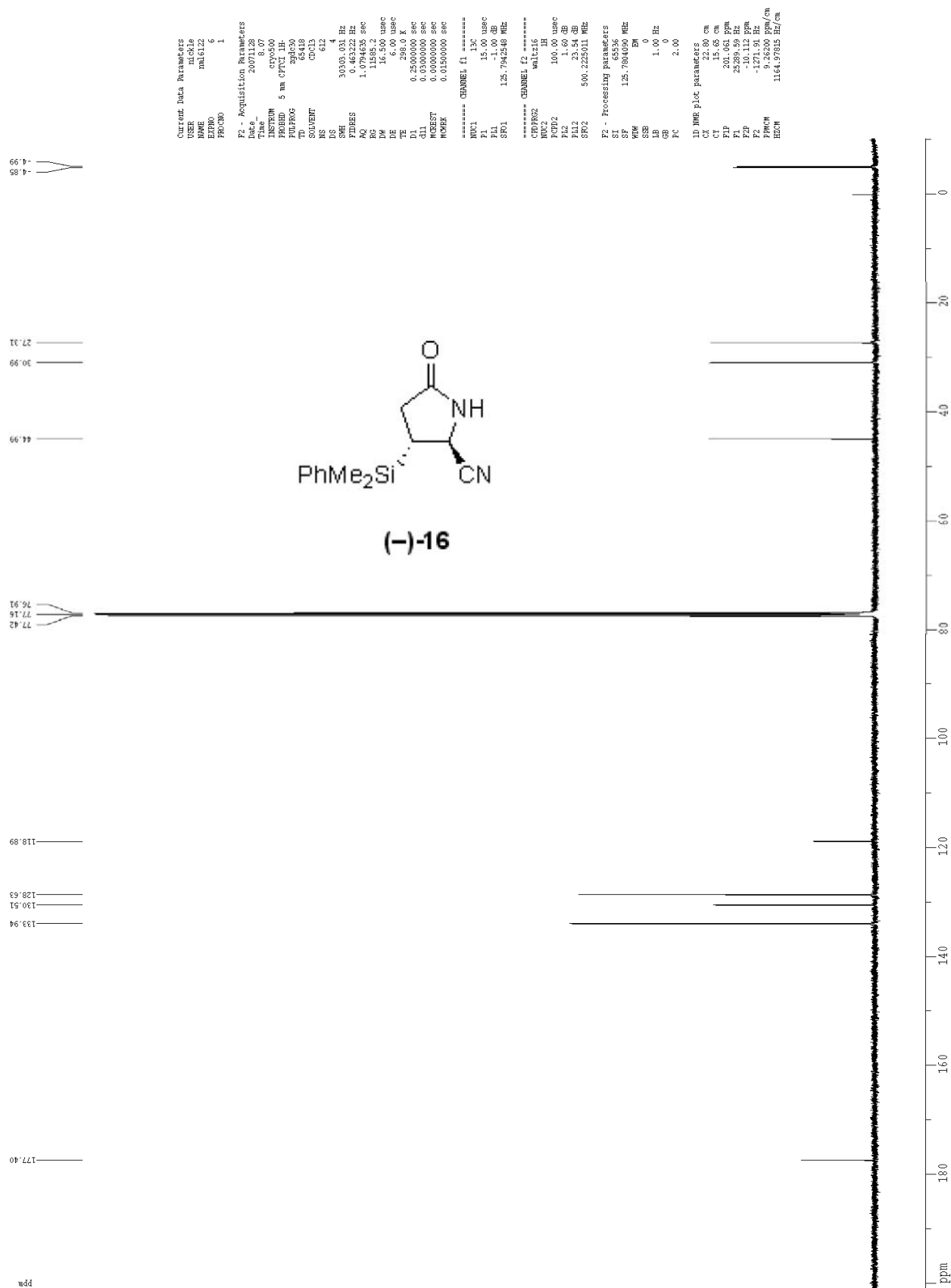


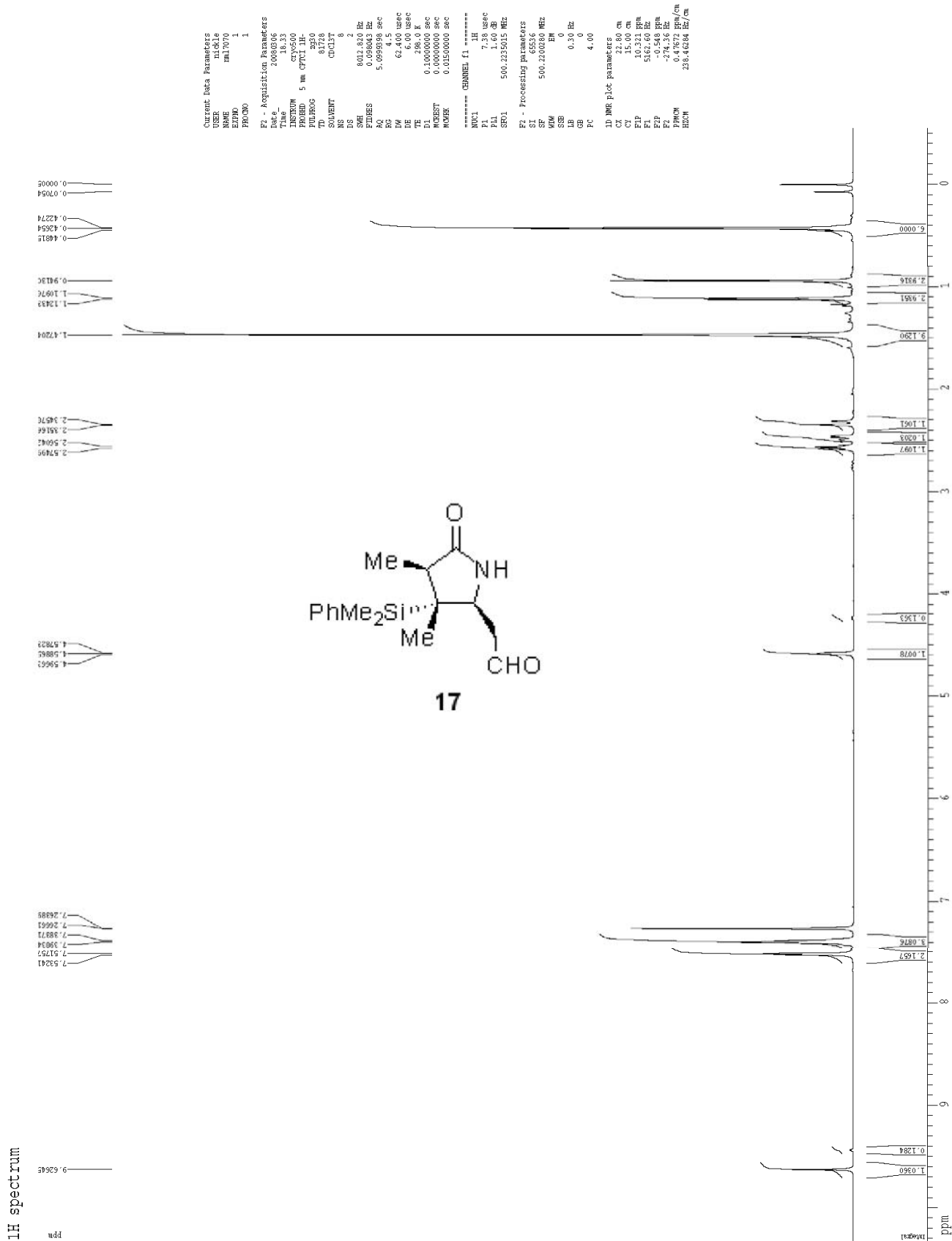
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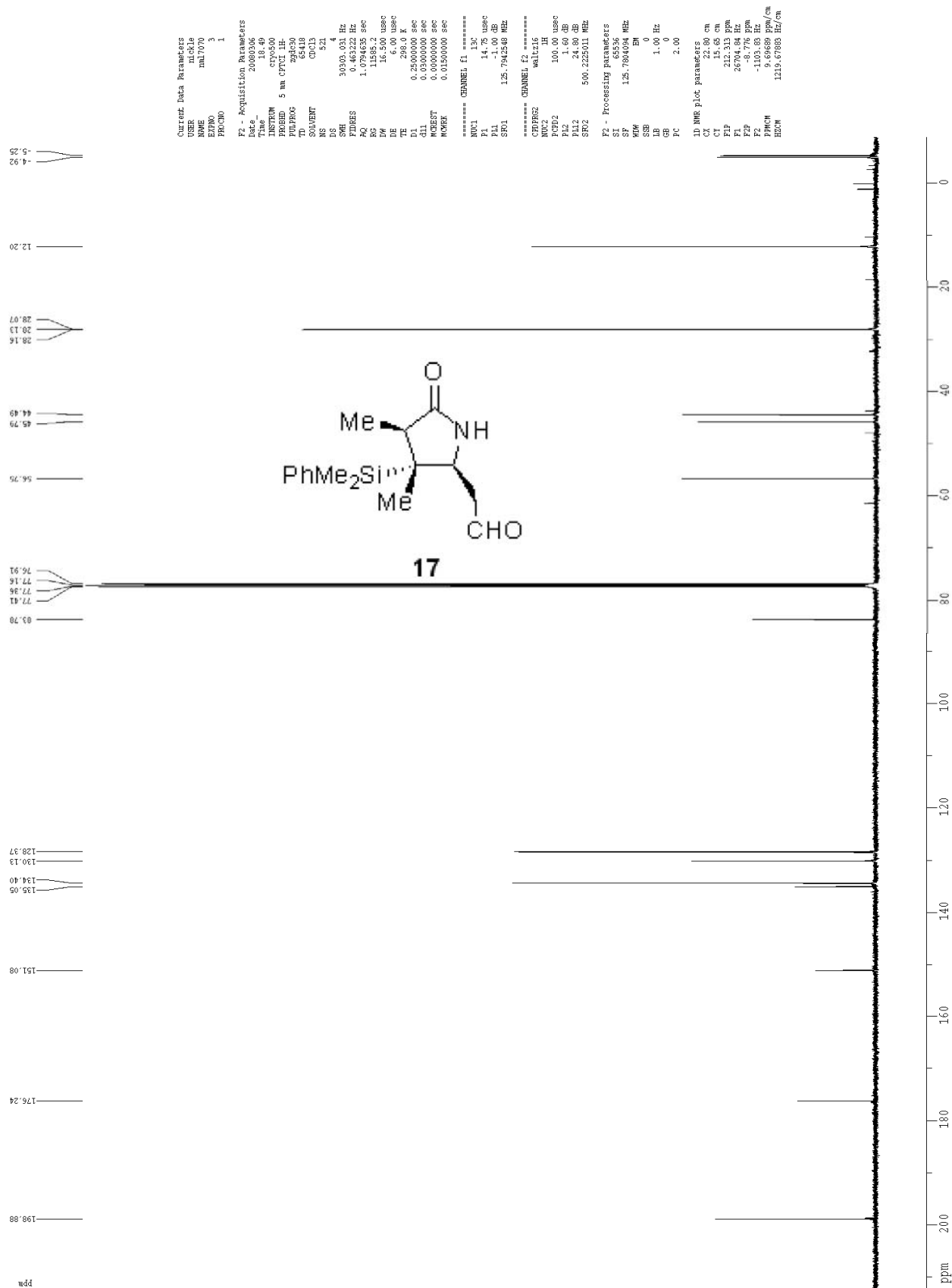






¹³C spectrum with ¹H decoupling



¹³C spectrum with ¹H decoupling

¹H spectrum

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7.26225

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2.51005

2.49215

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1.64475

1.49551

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1.27737

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0.99505

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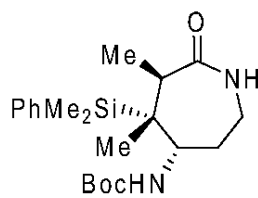
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18

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 FWHM 0.36205 ppm/cm
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P1 12.00 usec

P11 0.00 dB

SFO1 400.1328009 MHz

F2 - Processing Parameters

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1D NMR plot parameters

CX 22.80 cm

CY 15.00 cm

F1 7.906 ppm

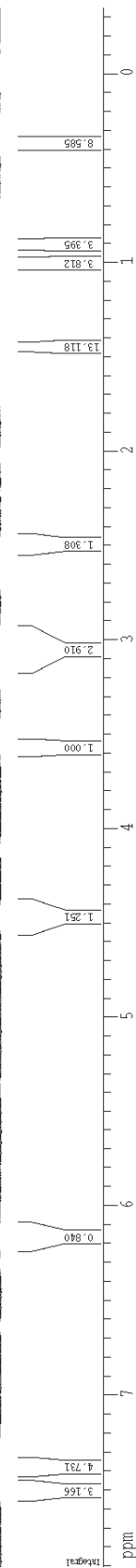
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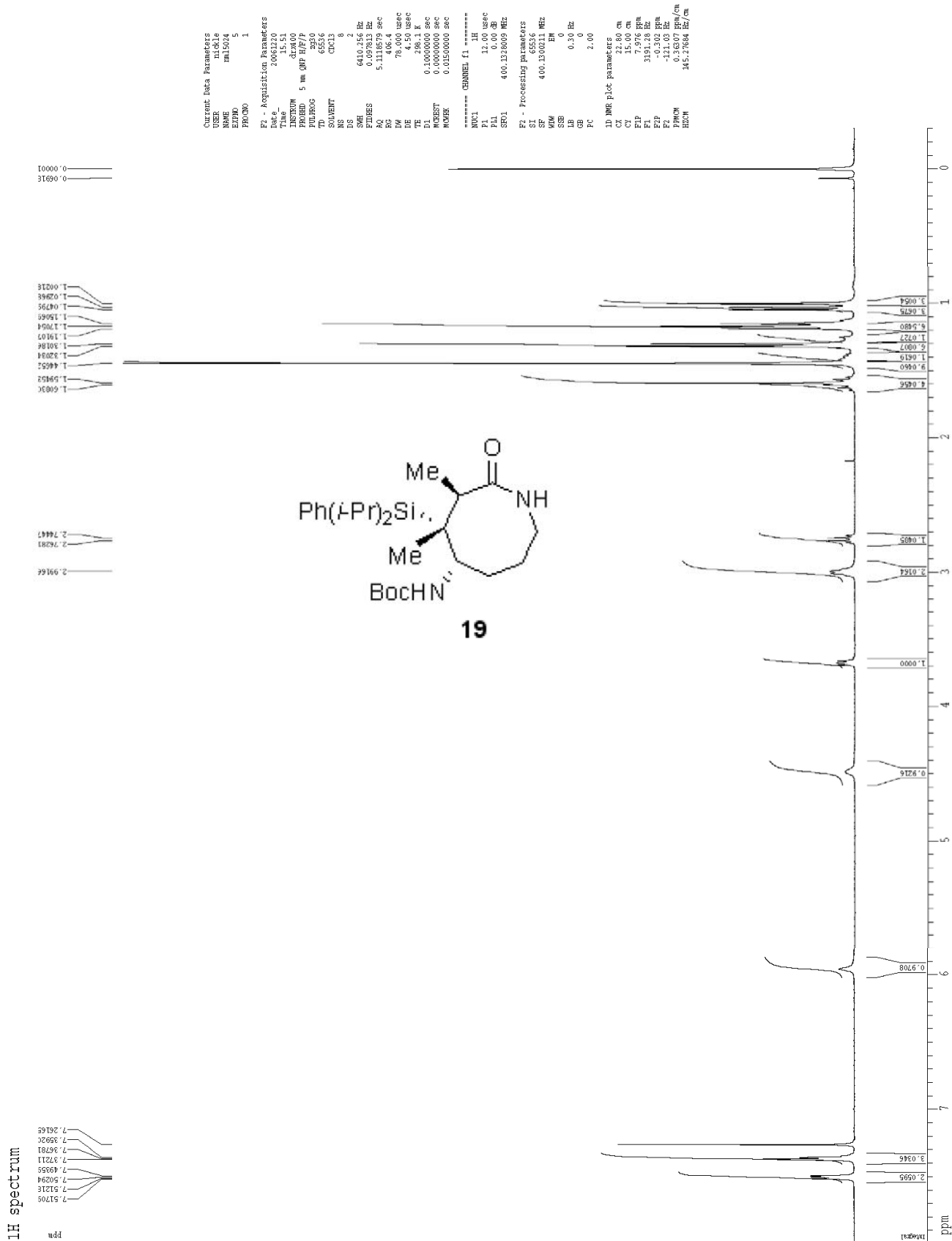
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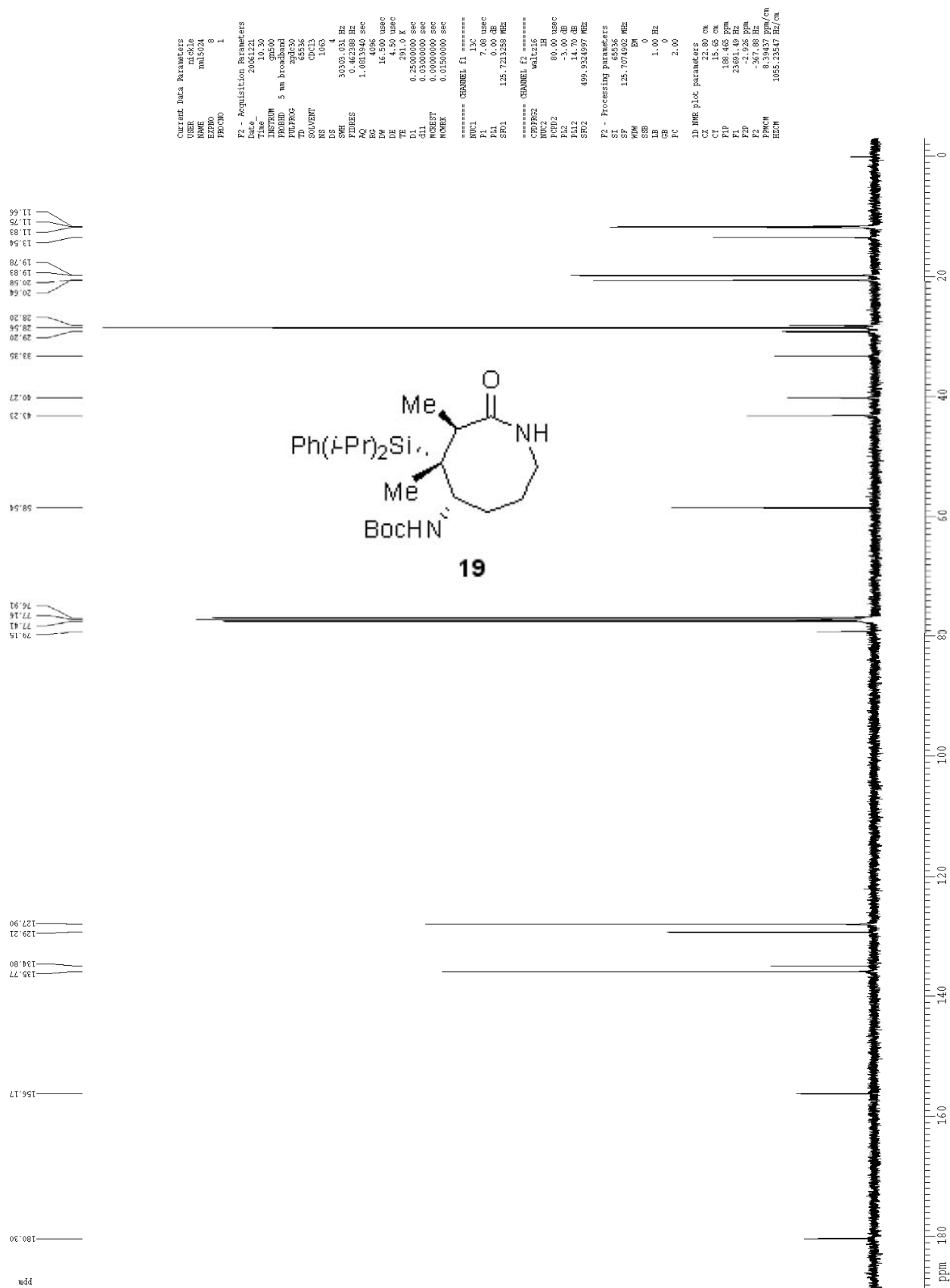
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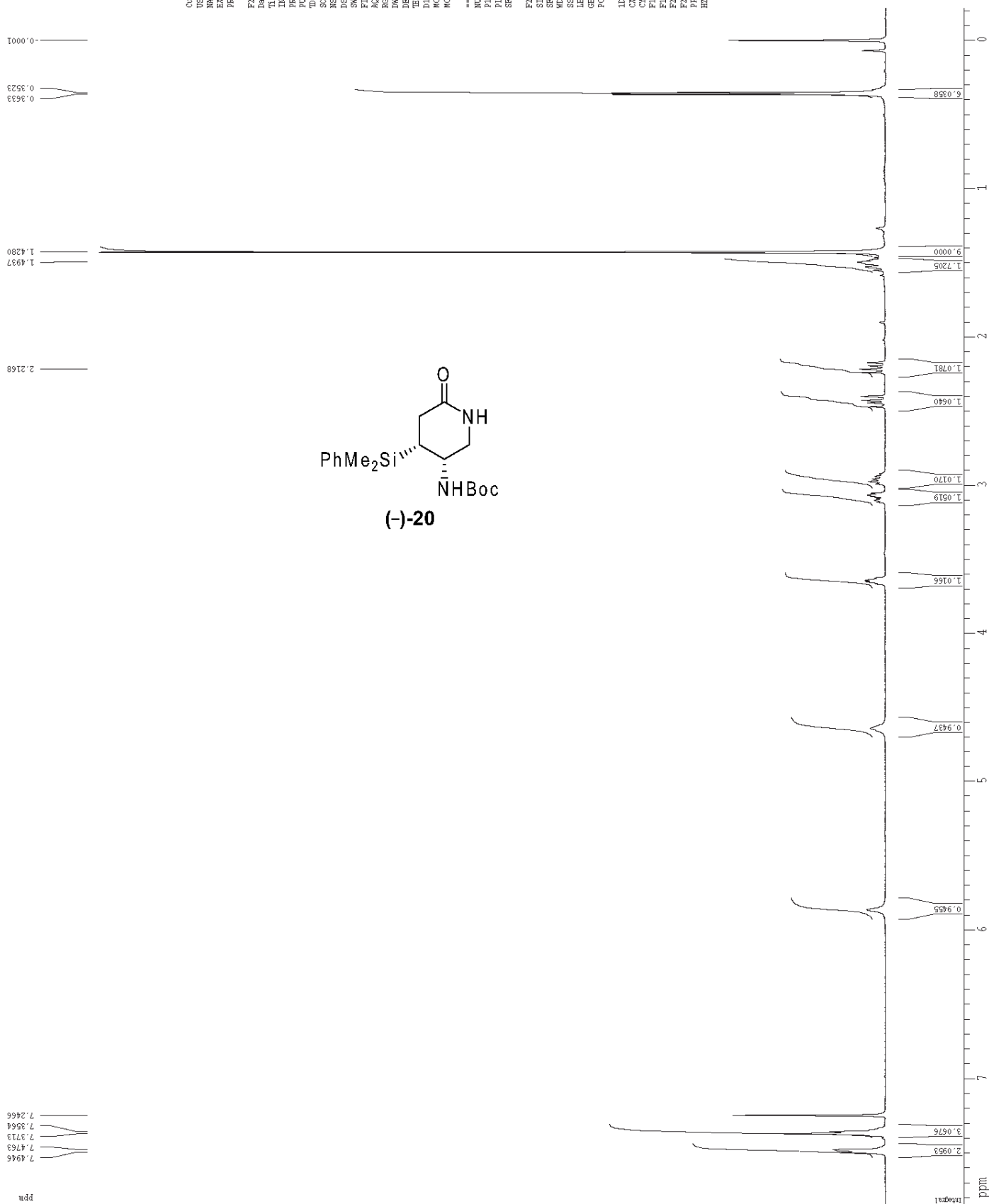
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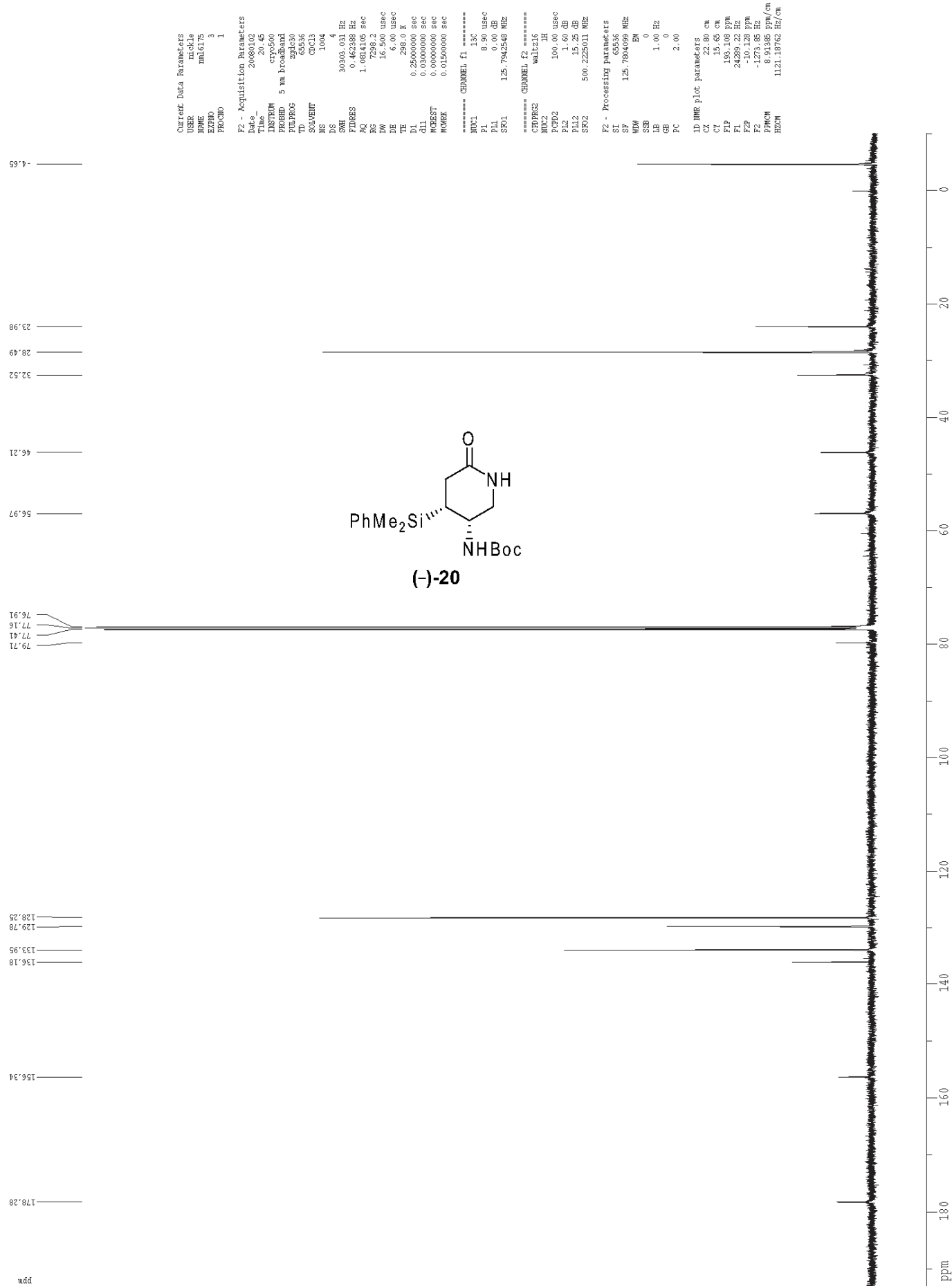
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¹³C spectrum with ¹H decoupling

¹H spectrum

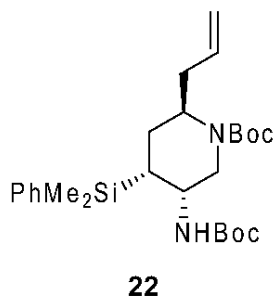
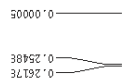
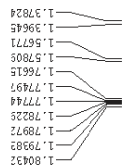
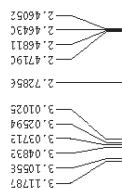
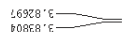
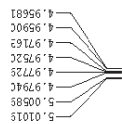
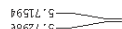
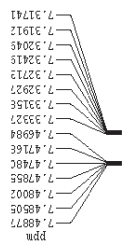
¹³C spectrum with ¹H decoupling

¹H spectrum

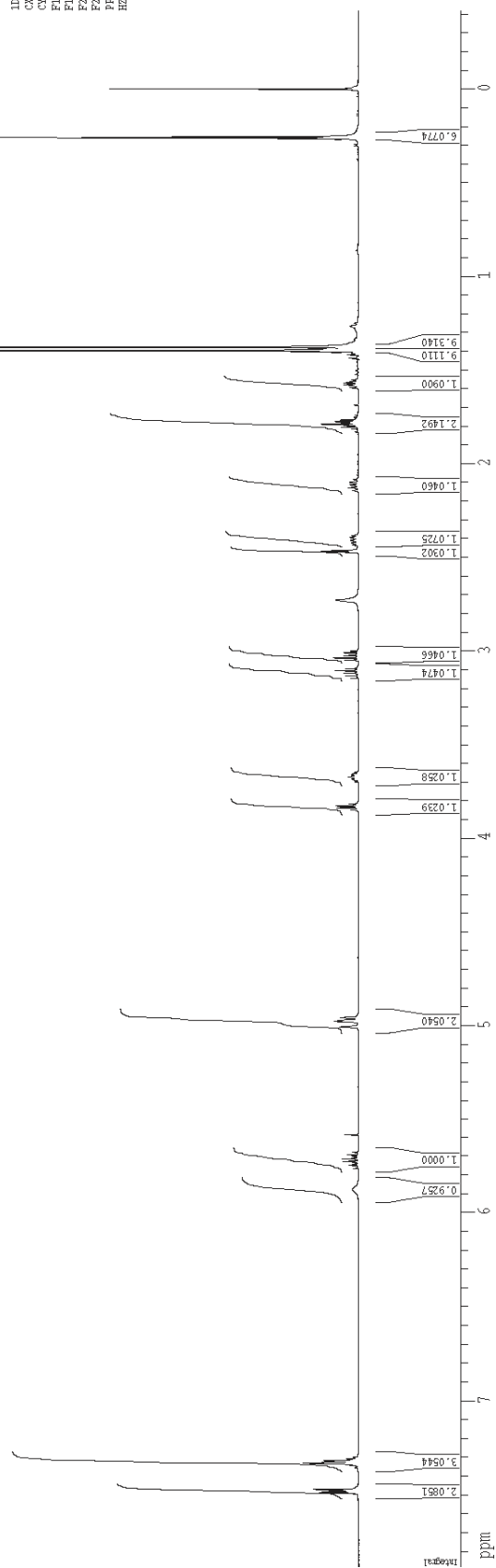
13C spectrum with 1H decoupling

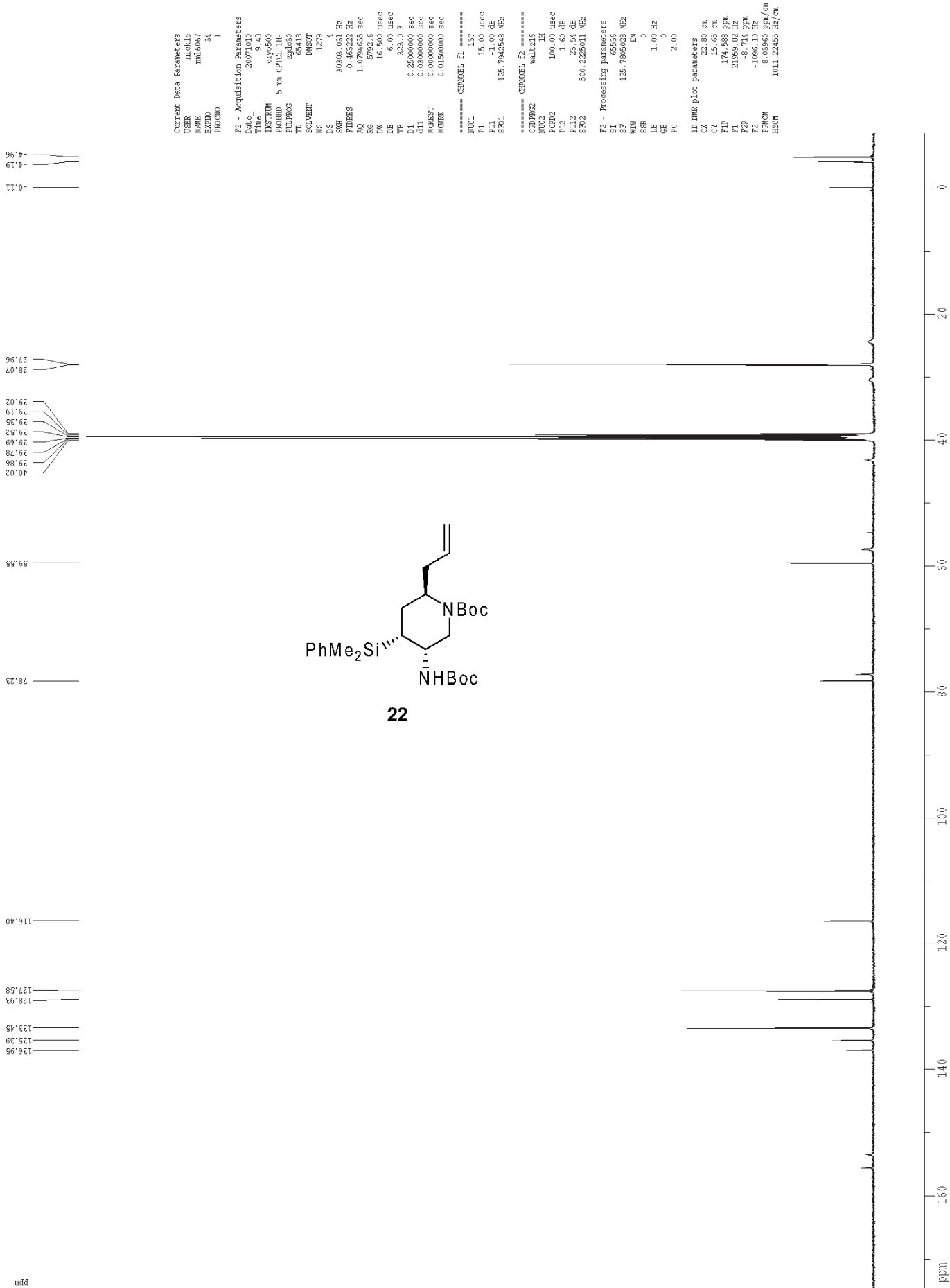


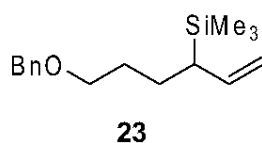
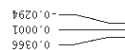
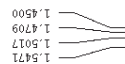
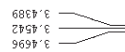
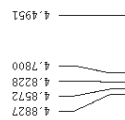
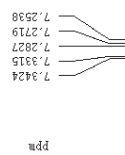
1H spectrum



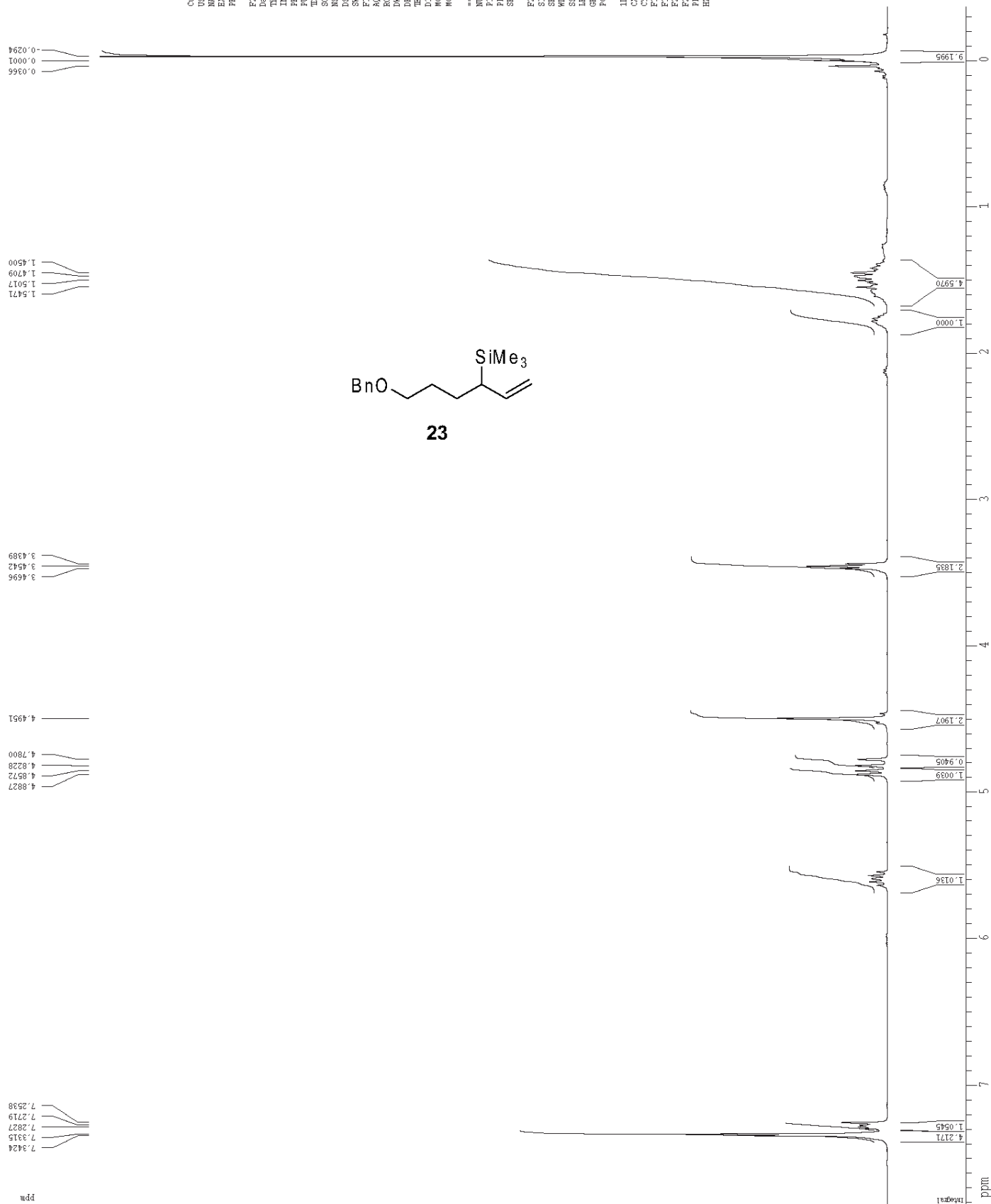
Current Data Parameters
 USER nickie
 NAME 20071010
 EXPNO 2
 PROCNO 1
 F2 - Acquisition Parameters
 Date_ 20071010
 Time 8.07
 INSTRUM gms500
 PROBHD 5 mm broadband
 PULPROG zgpg30
 TD 65536
 SFO1 400.146098 MHz
 SOLVENT DMSO-D
 NS 8
 DS 2
 SWH 8402.810 Hz
 FIDRES 0.098043 Hz
 AQ 5.0998774 sec
 RG 724.1
 DW 62.400 usec
 DE 6.00 usec
 TE 300.2 K
 T1 3.00 sec
 T1RHO 0.1000000 sec
 NOEST 0.0000000 sec
 NOEXET 0.0150000 sec
 ===== CHANNEL f1 =====
 NUC1 1H
 P1 12.00 usec
 PL1 -3.00 dB
 SFO1 400.146098 MHz
 F2 - Processing parameters
 SI 65536
 SF 499.8250279 MHz
 WDM EM
 SSF 0
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 4.00
 1D NMR Plot Parameters
 CX 22.80 cm
 CY 15.00 cm
 F1F 7.882 ppm
 F1 3939.83 Hz
 F2F -0.419 ppm
 F2 -209.31 Hz
 FWHM 0.36409 ppm/cm
 HZCM 181.97949 Hz/cm

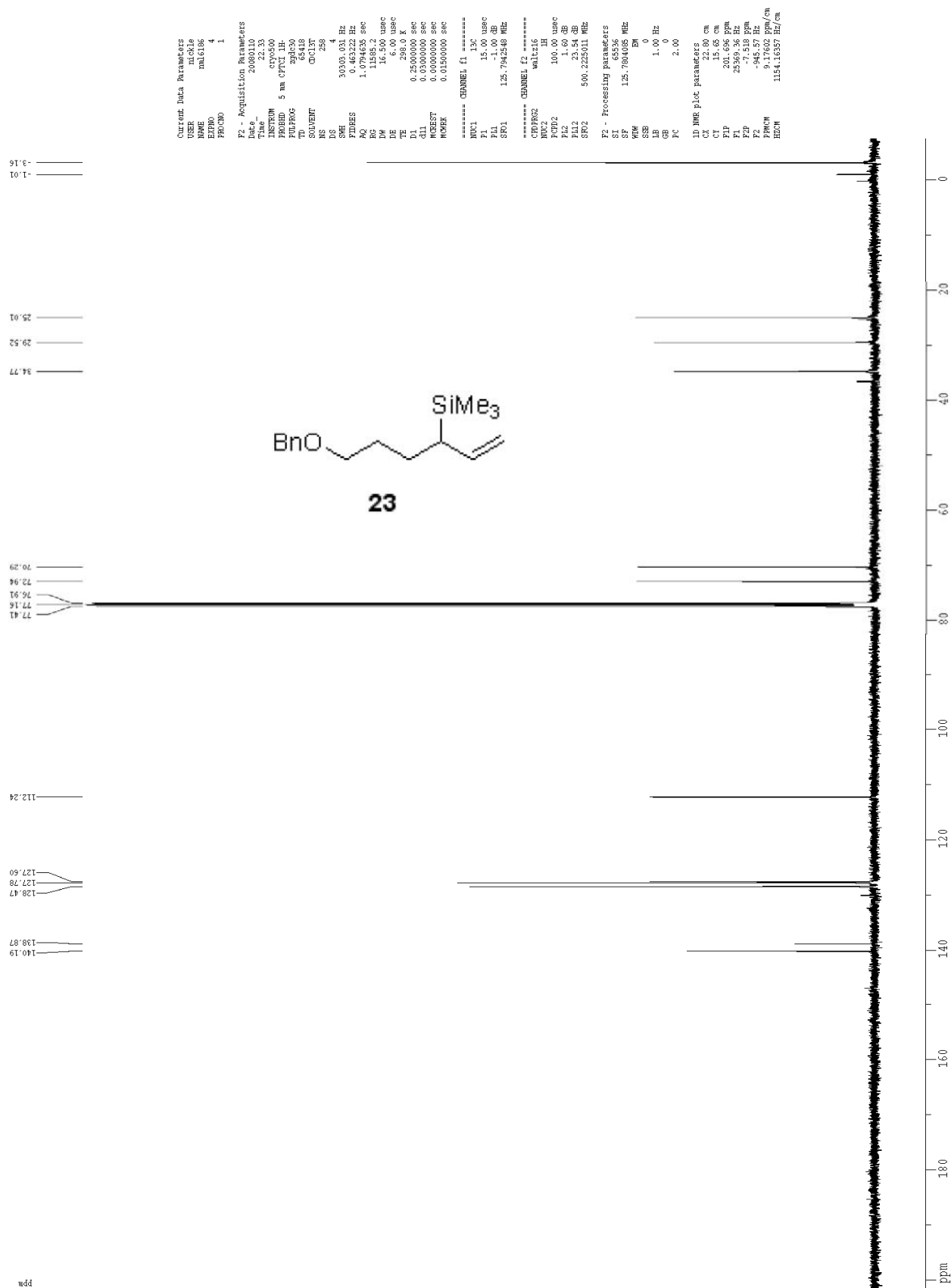


¹³C spectrum with ¹H decoupling

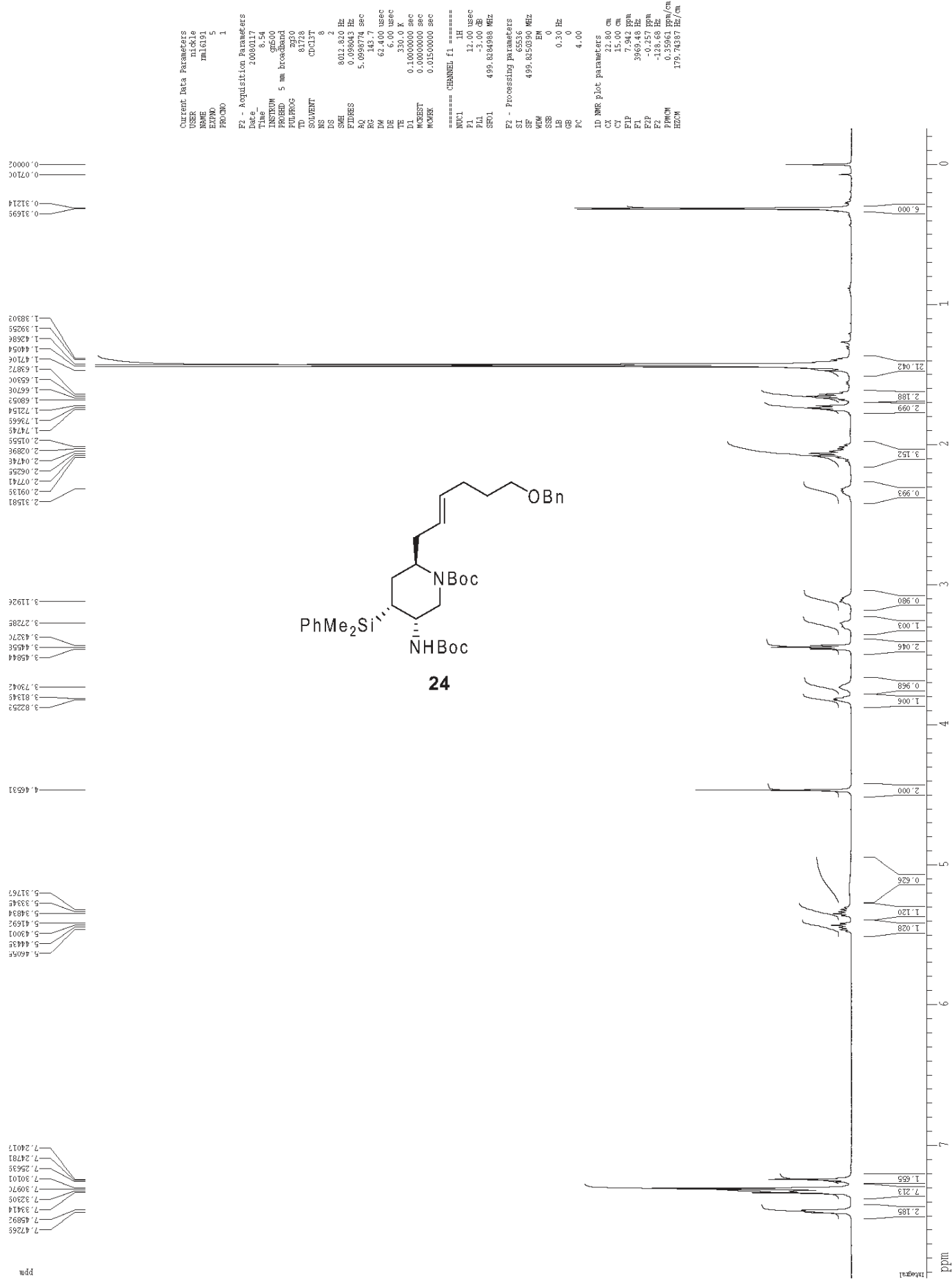
¹H spectrum

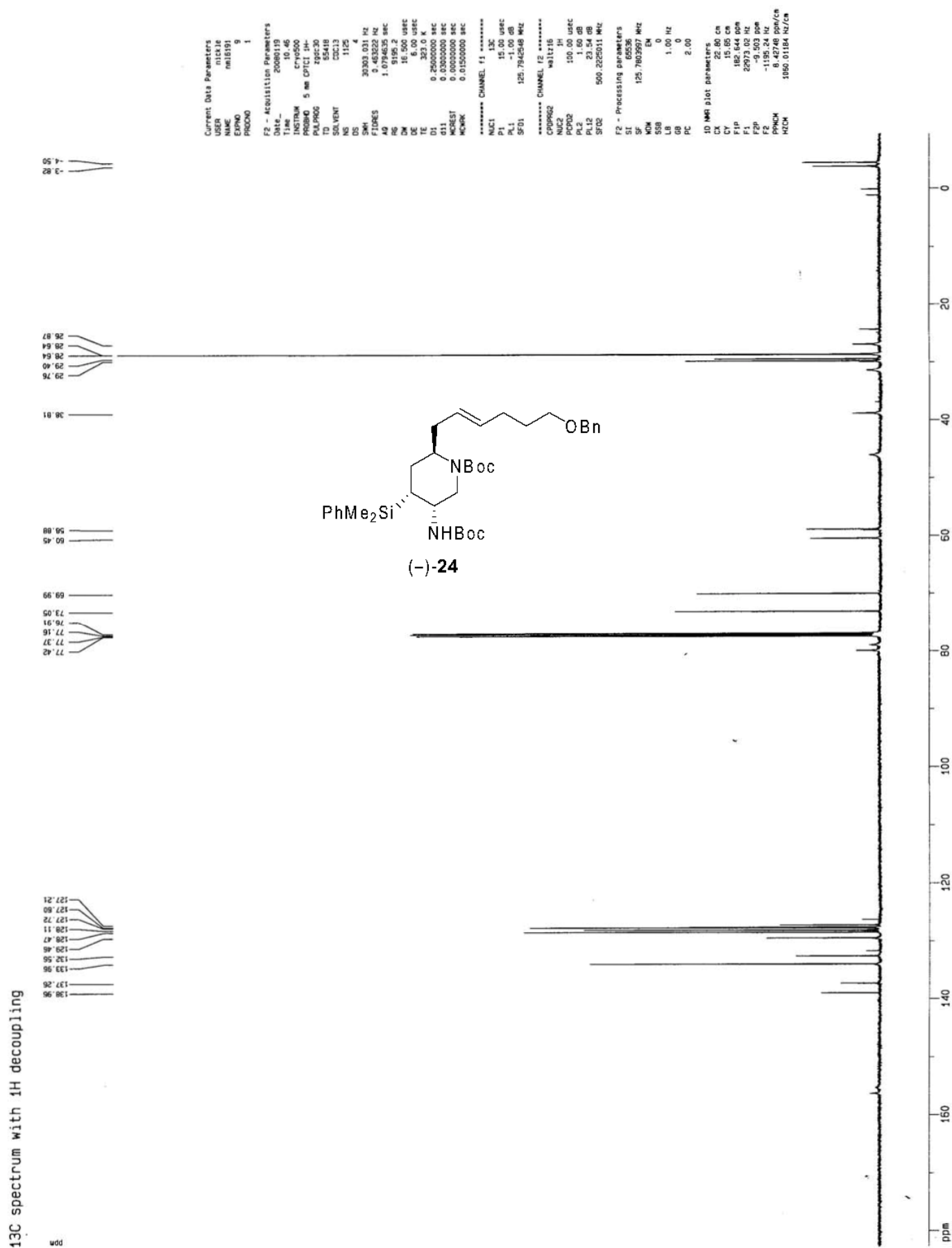
Current Data Parameters
 USER nickle
 NAME nm16186
 ACQNO 1
 PROCNO 1
 F2 - Acquisition Parameters
 Date 20080103
 Time 16.29
 INSTRUM dxt400
 PROHD 5 mm QNP H/F/P
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 2
 DS 2
 SWH 6410.256 Hz
 FIDRES 0.097813 Hz
 AQ 5.1118579 sec
 RG 203.2
 DW 78.000 usec
 DE 4.50 usec
 TE 297.9 K
 D1 0.10000000 sec
 MCHST 0.00000000 sec
 MCHPK 0.01500000 sec
 ===== CHANNEL f1 =====
 NUCL1 1H
 P1 12.00 usec
 PL1 0.00 dB
 SFO1 400.1328009 MHz
 F2 - Processing parameters
 SI 65536
 SF 400.1328009 MHz
 RG 1
 SSF 0
 LB 0.30 Hz
 GB 0
 PC 2.00
 1D NMR plot parameters
 CX 22.80 cm
 CY 15.00 cm
 FIP 7.808 ppm
 FL 3124.16 Hz
 F2 4.00 ppm
 F3 -147.34 Hz
 PPM0W 0.35860 ppm/cm
 HZ0W 143.48653 Hz/cm



¹³C spectrum with ¹H decoupling

1H spectrum





¹H spectrum

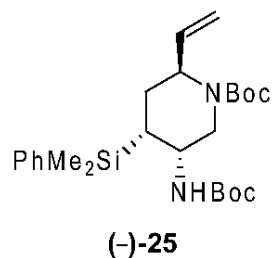
ppm

7.4812
7.4765
7.4637
7.4576
7.3294
7.3230
7.3130

2.7932
2.4806
2.4795
2.4712
2.4665
2.4617

1.4032
1.3922
1.3731
1.3675
1.3596

0.2545
0.2452
0.2321
0.2166
0.1973
0.1762
0.0001



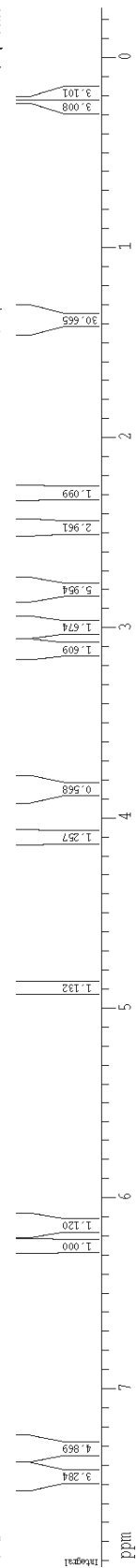
Current Data Parameters
 USER nickie
 NAME 20080416
 EXPNO 4
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20080416
 Time 10.47
 INSTRUM dr400
 PROBD 5 mm QNP H/F/P
 PULPROG zgpg30
 TD 65536
 SFO1 400.1328009 MHz
 SOLVENT DMSO-d₆
 NS 8
 DS 2
 SWH 6410.256 Hz
 FIDRES 0.097813 Hz
 AQ 5.1118579 sec
 RG 456.1
 DW 78.000 usec
 DE 4.50 usec
 TE 300.2 K
 T1 0.10000000 sec
 T1RHO 0.00000000 sec
 NOEST 0.00000000 sec
 NOVER 0.01500000 sec

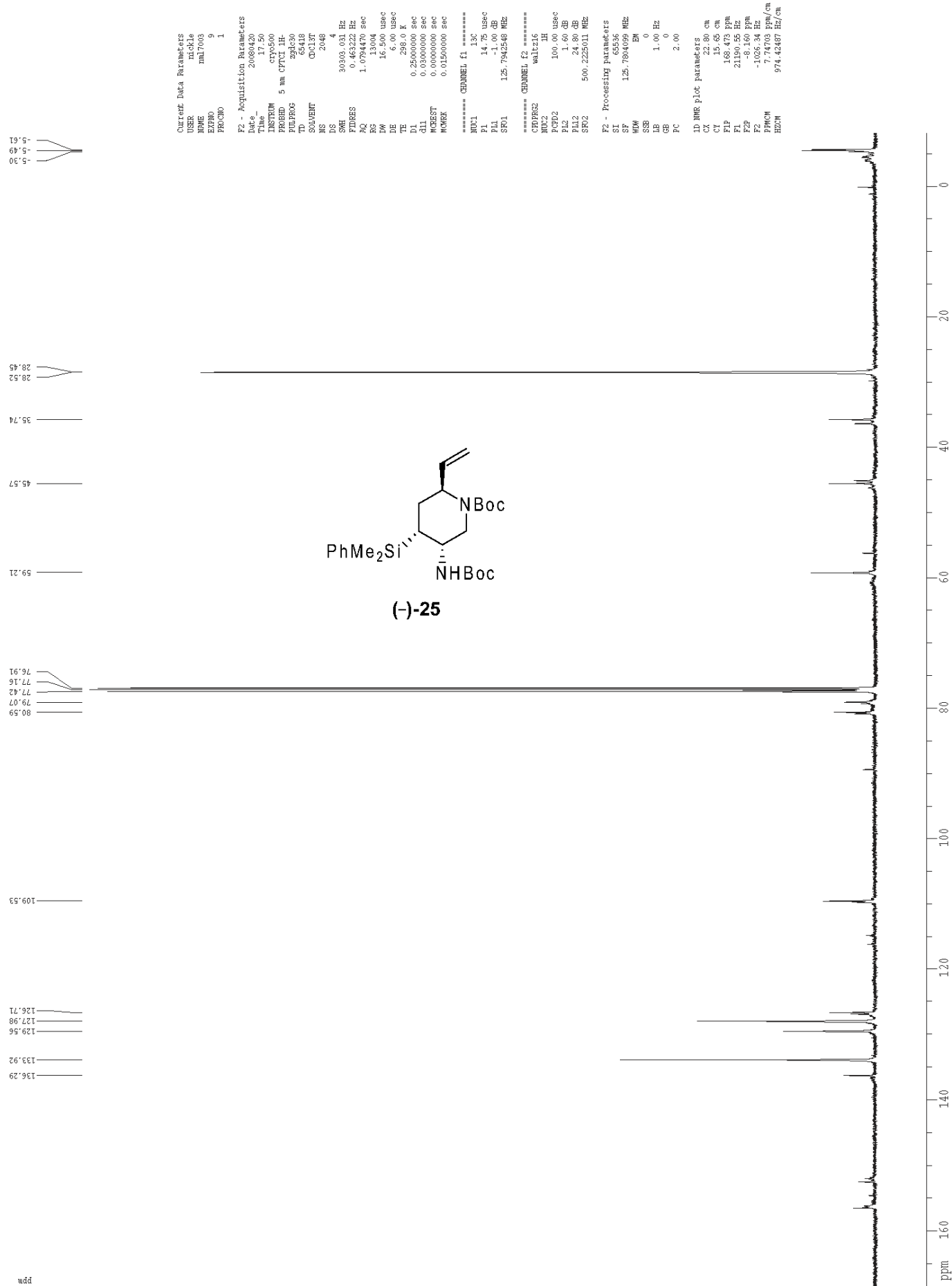
===== CHANNEL f1 =====
 NUC1 1H
 P1 12.00 usec
 PL1 0.00 dB
 SFO1 400.1328009 MHz

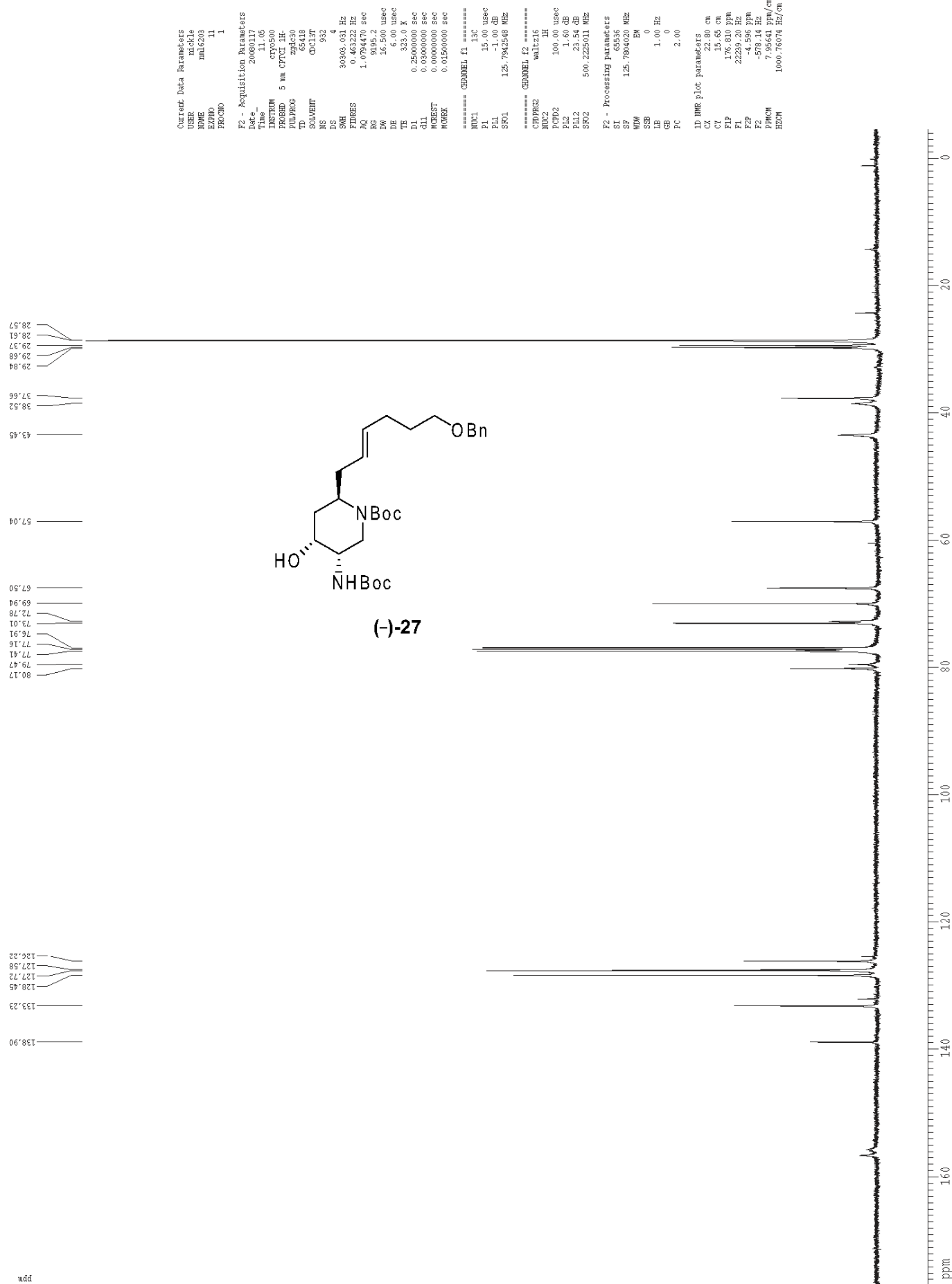
F2 - Processing parameters
 SI 65536
 SF 400.1300185 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 2.00

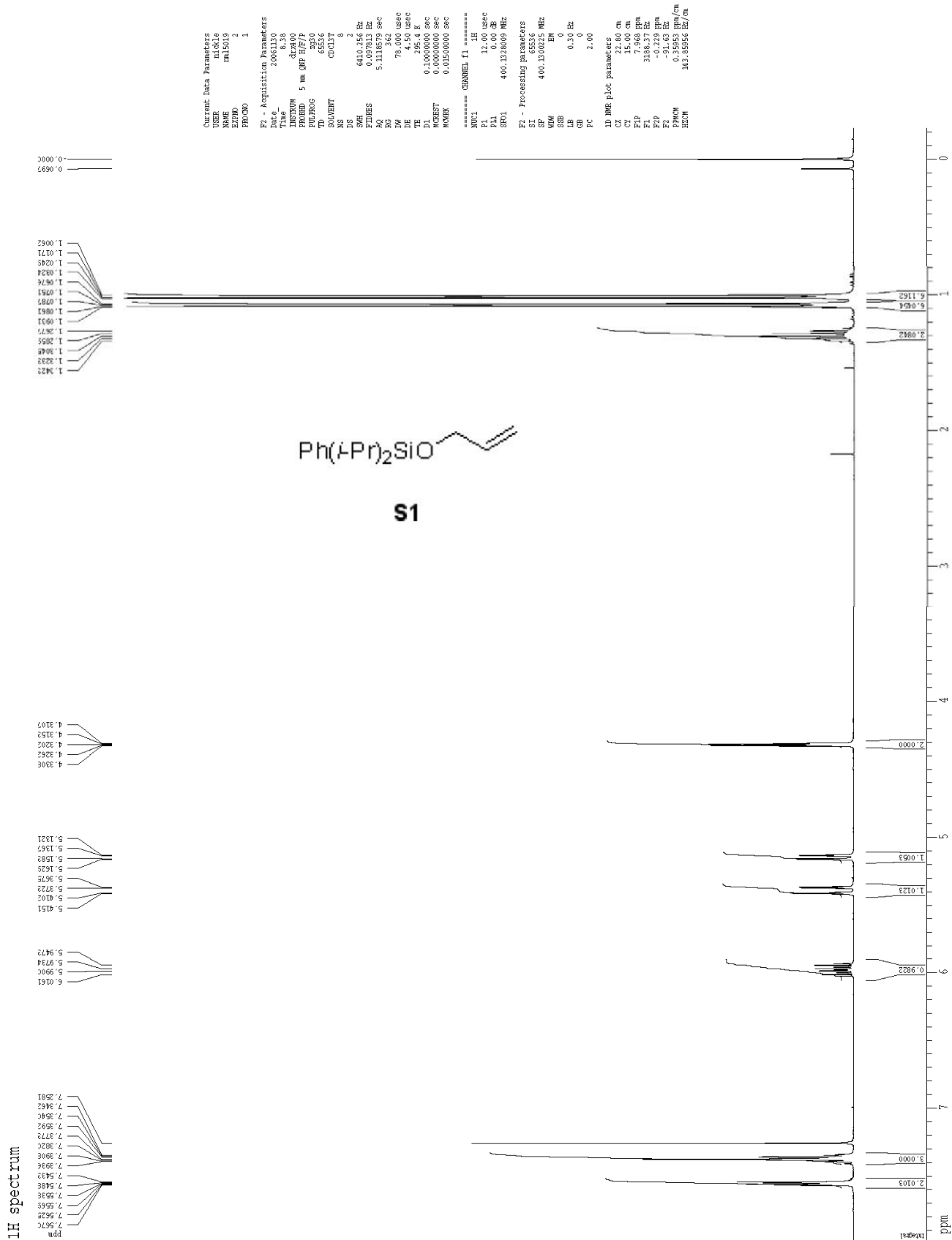
1D NMR plot parameters
 CX 22.80 cm
 CY 15.00 cm
 F1 7.932 ppm
 F2 3173.85 Hz
 F2P -0.262 ppm
 F2 -104.68 Hz
 FWHM 0.35927 ppm/cm
 HZCM 143.79509 Hz/cm

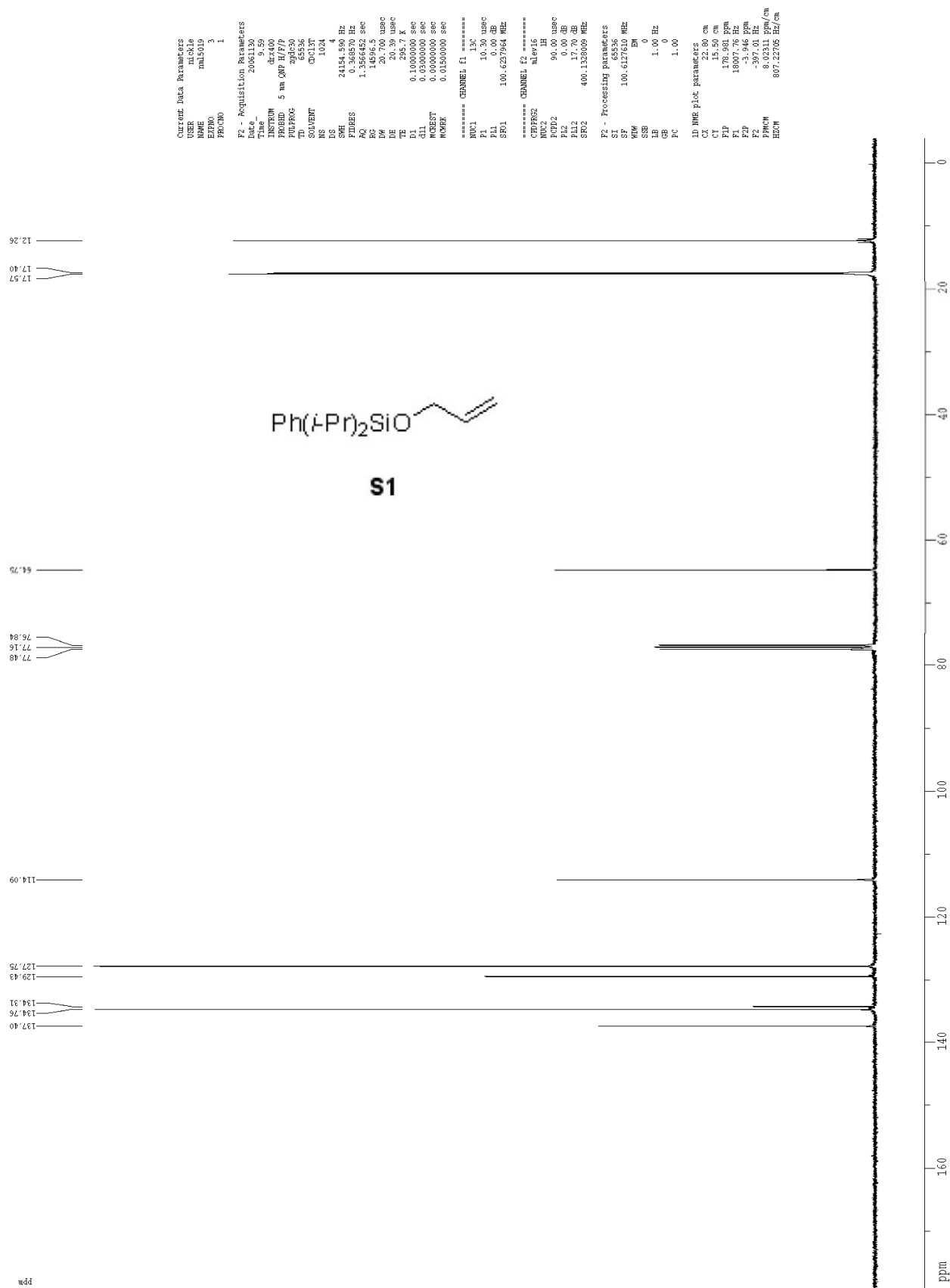


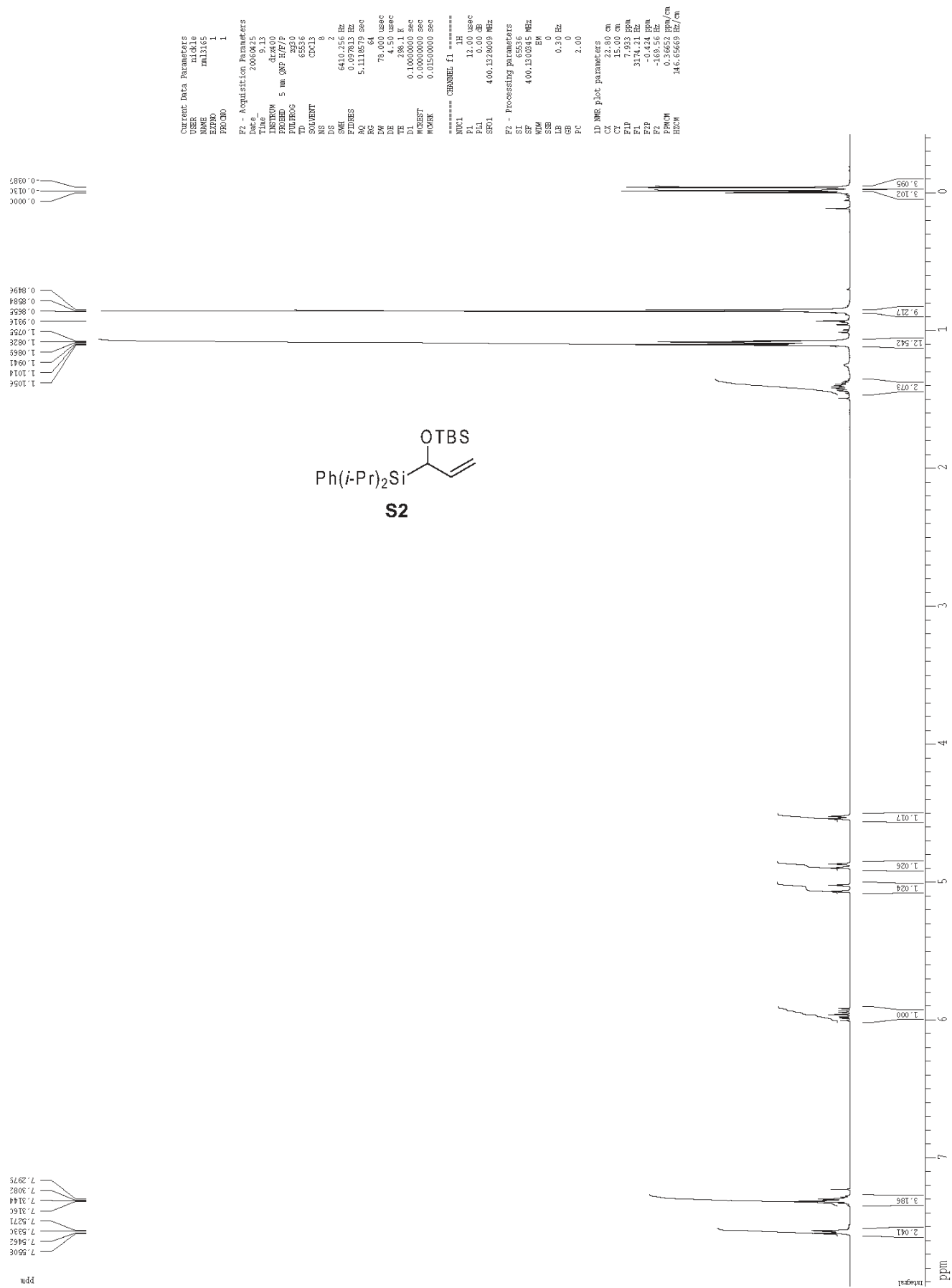
13C spectrum with 1H decoupling



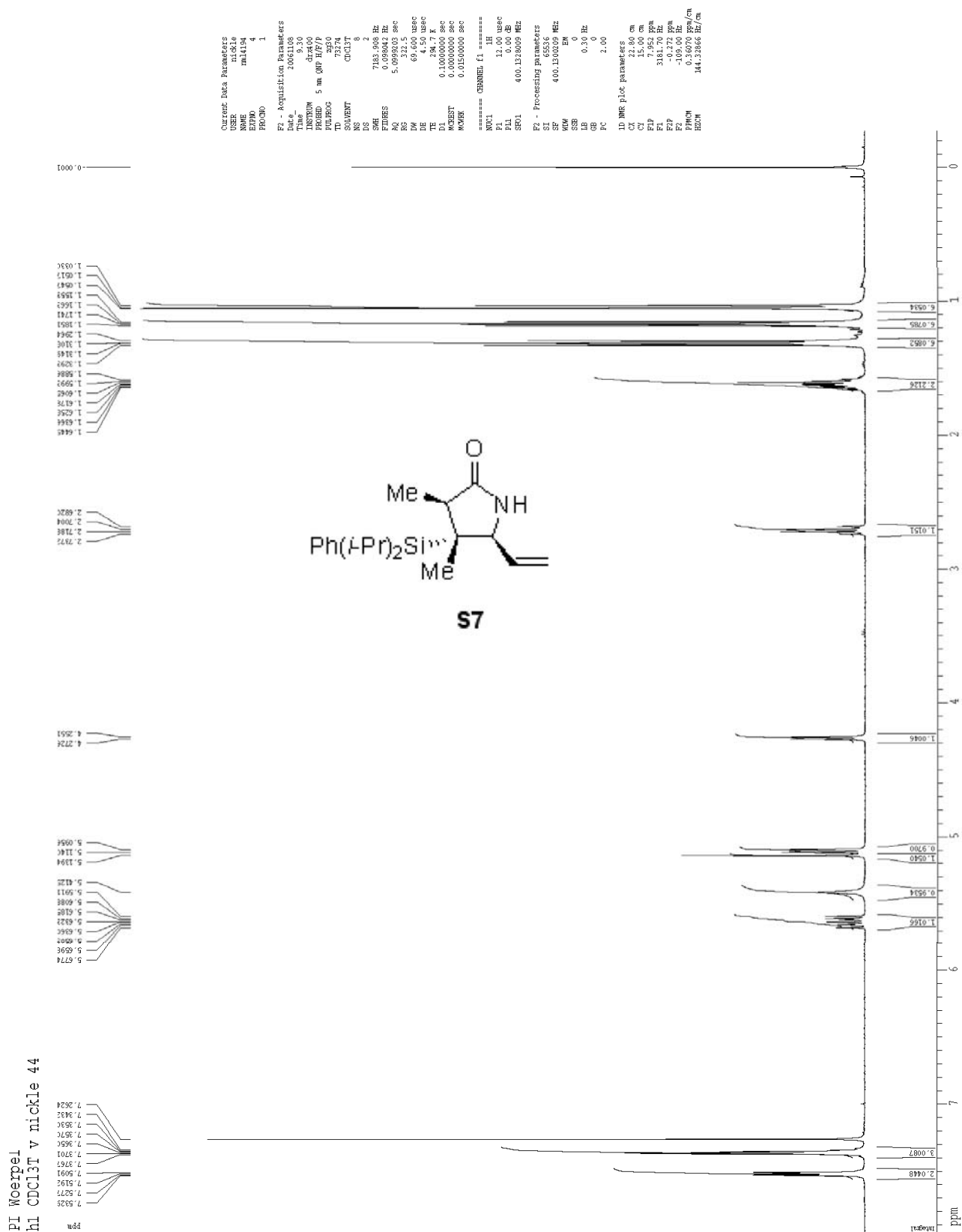
¹³C spectrum with ¹H decoupling

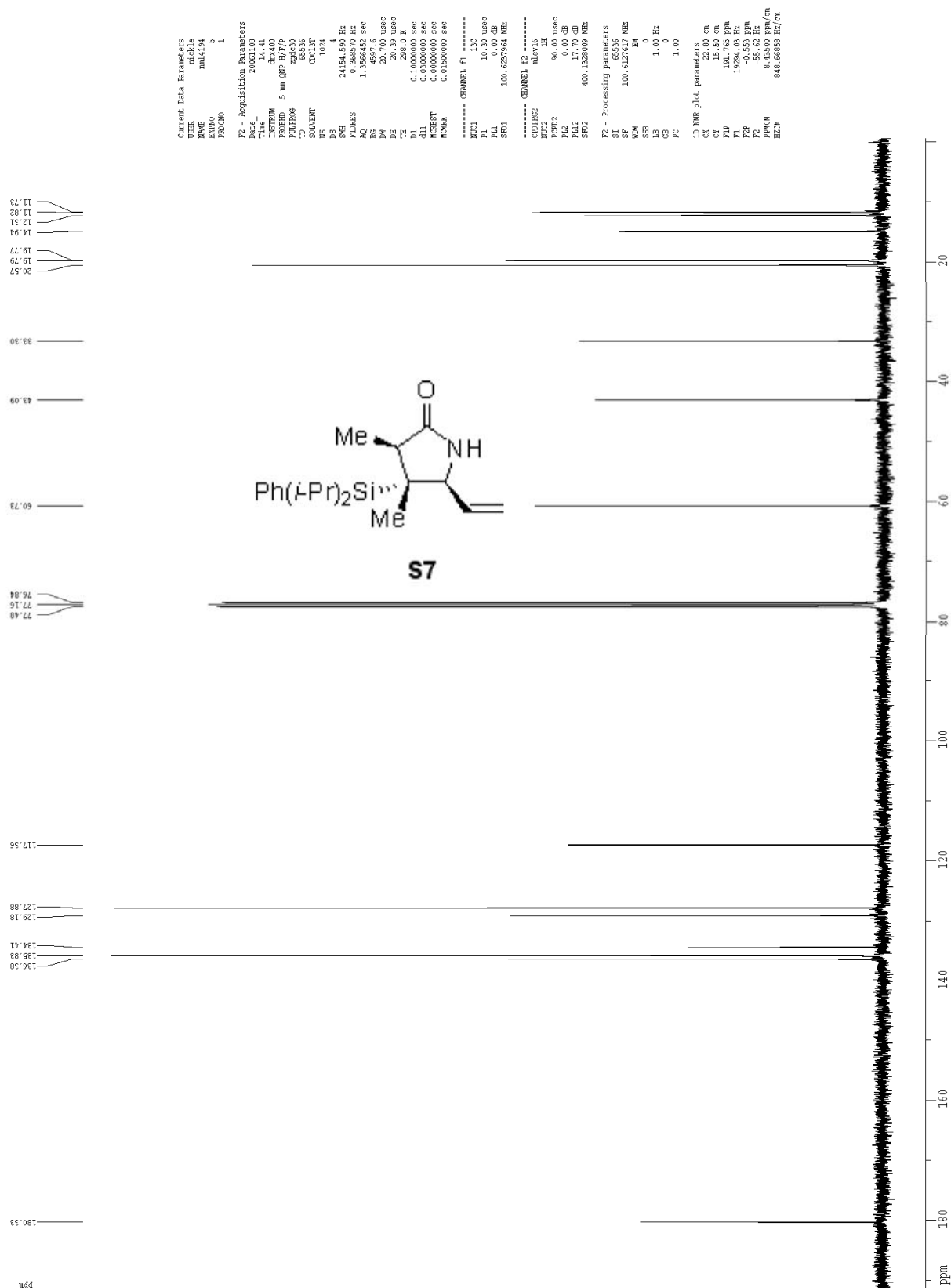


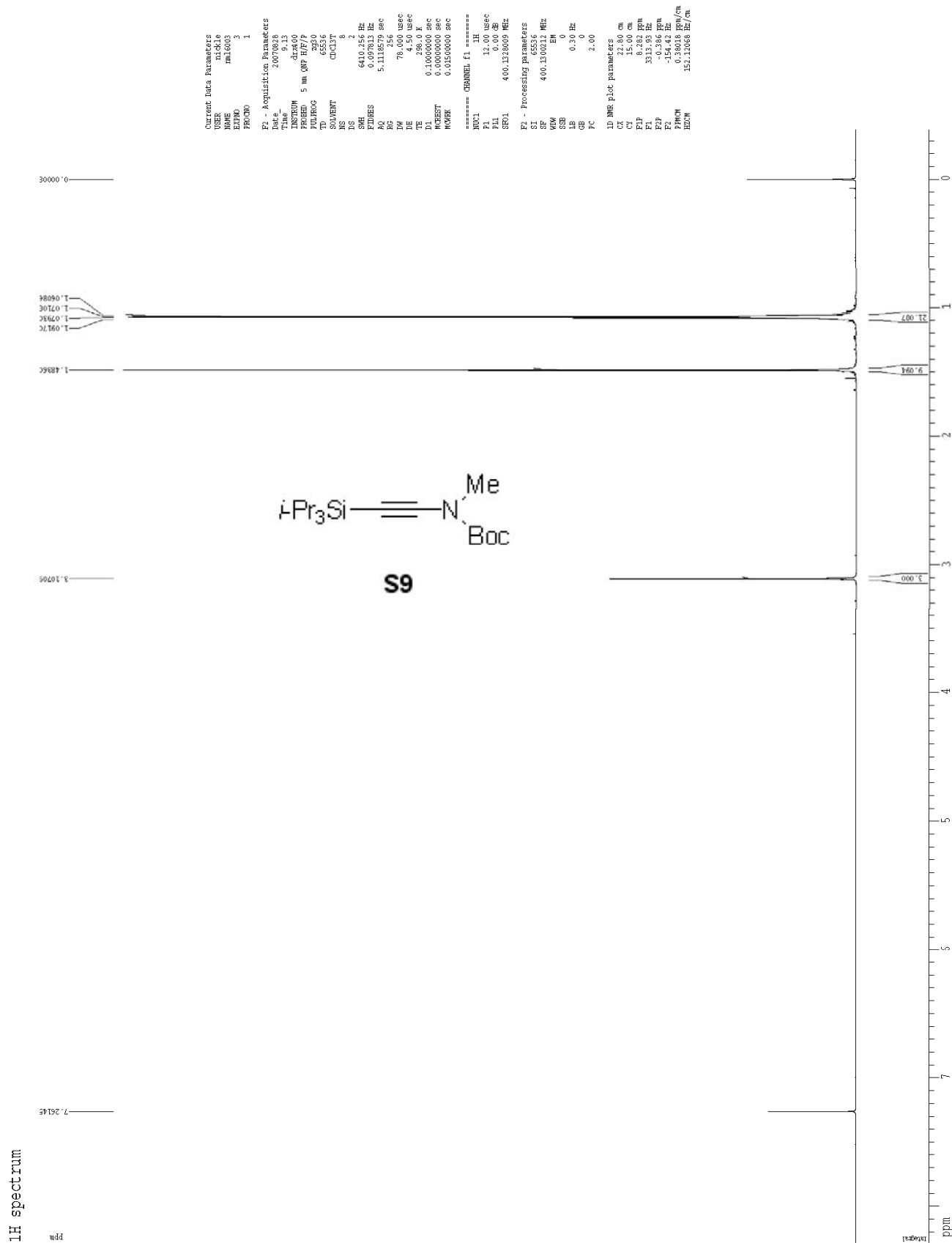
¹³C spectrum with ¹H decoupling

¹H spectrum

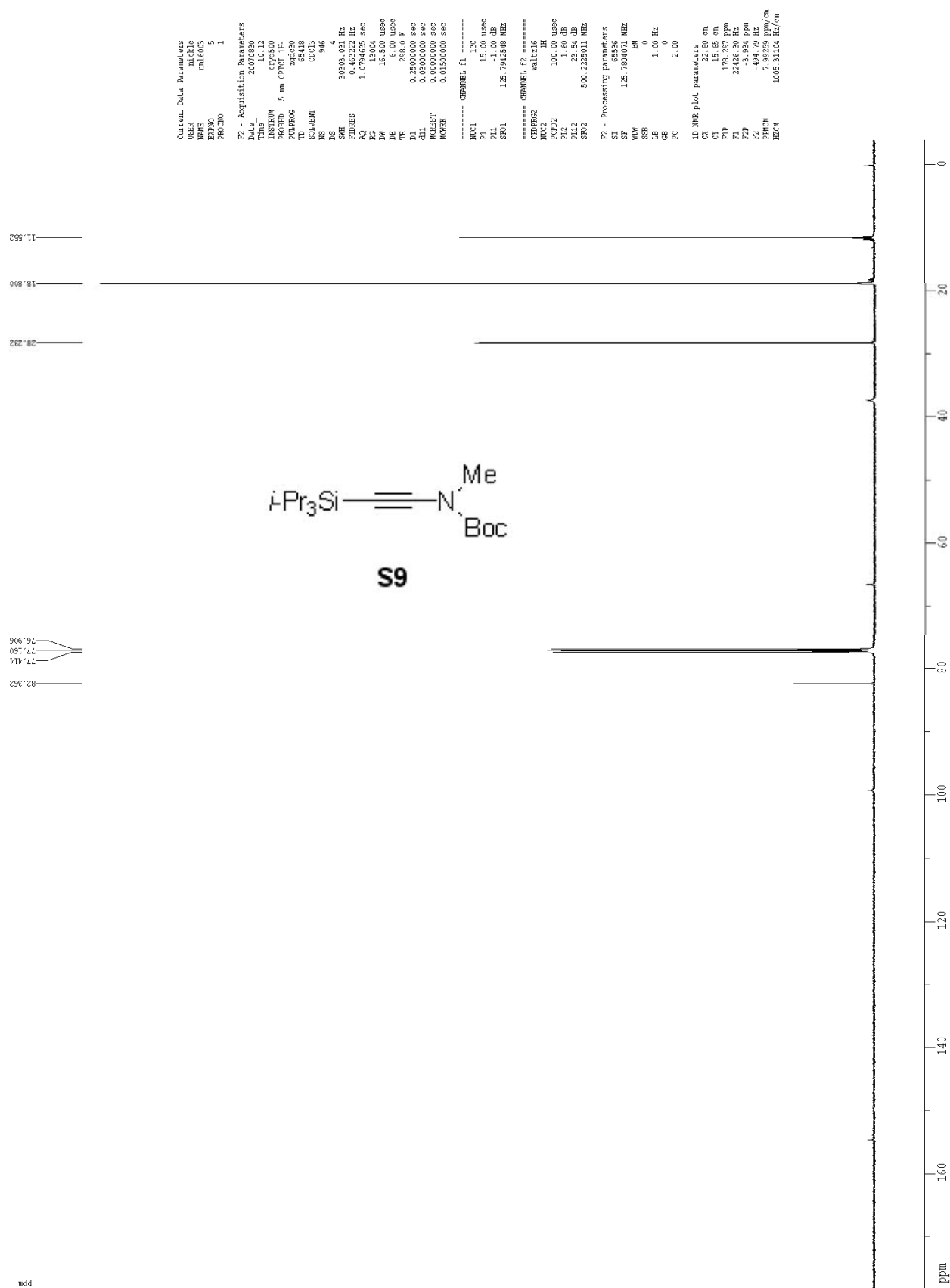
Note: Compound **S7** is an intermediate in the formation of azide **3** (Scheme 1.)

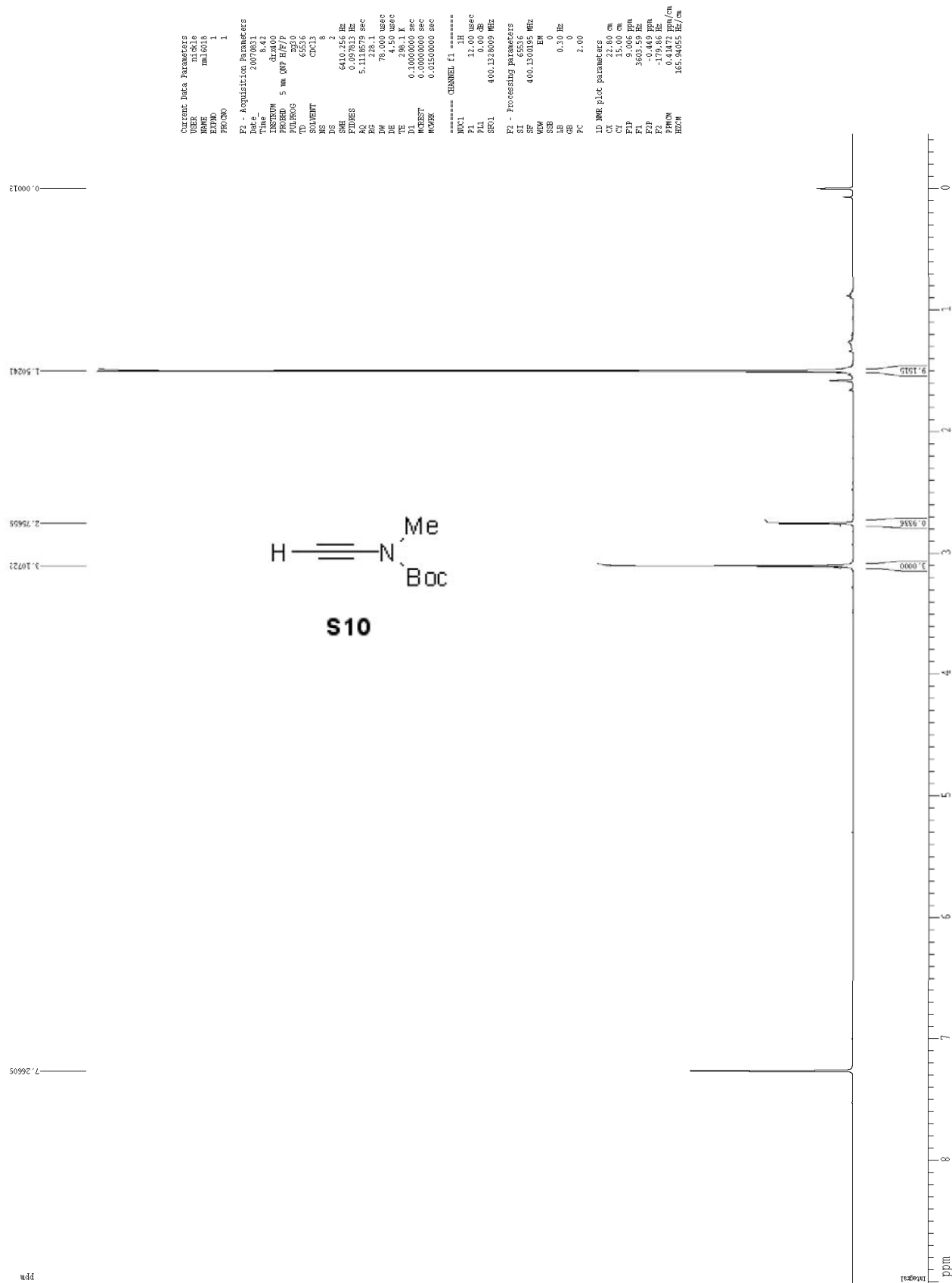


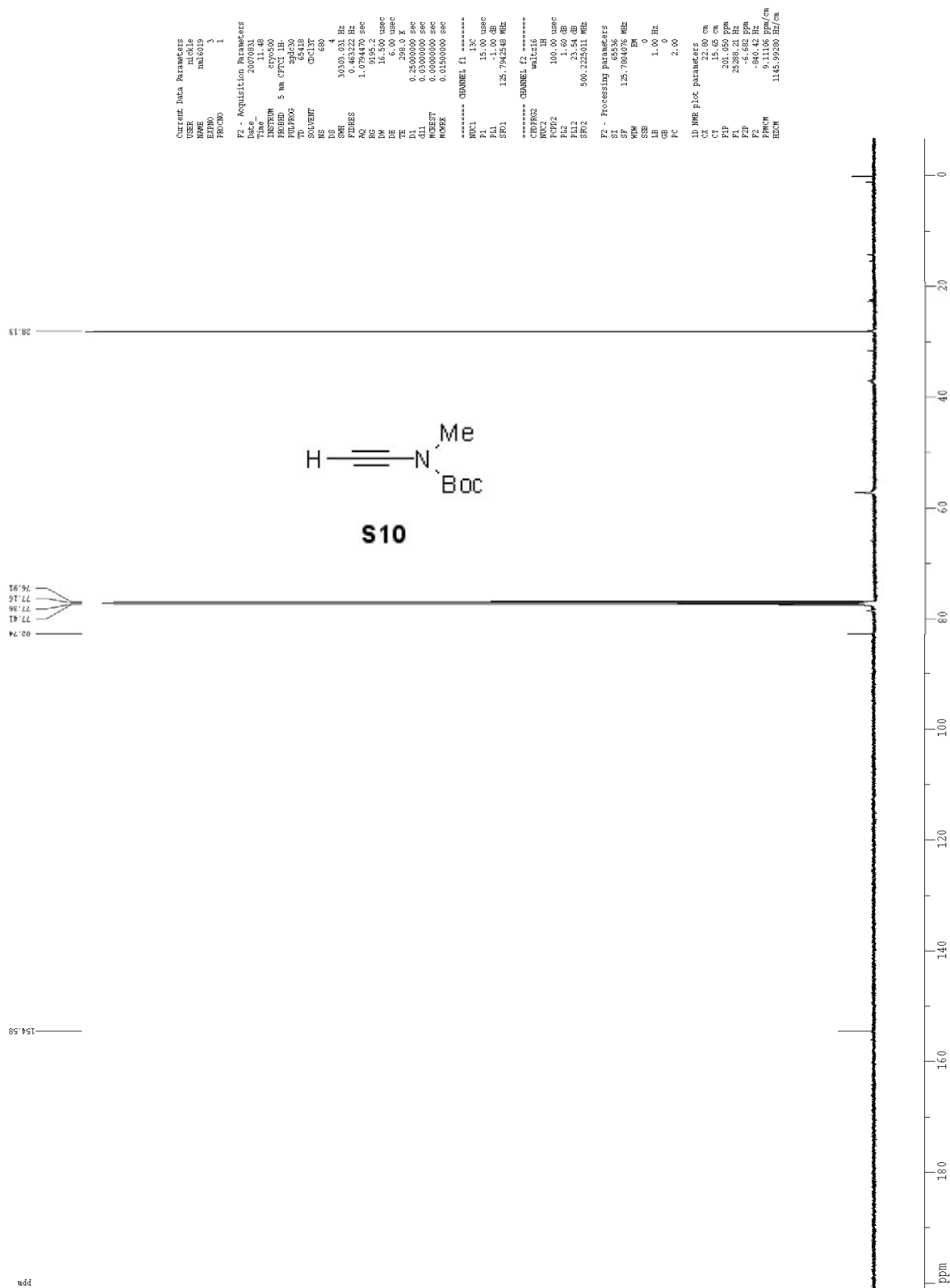
PI Woerpel
cl3 CDC13T v nickle 16

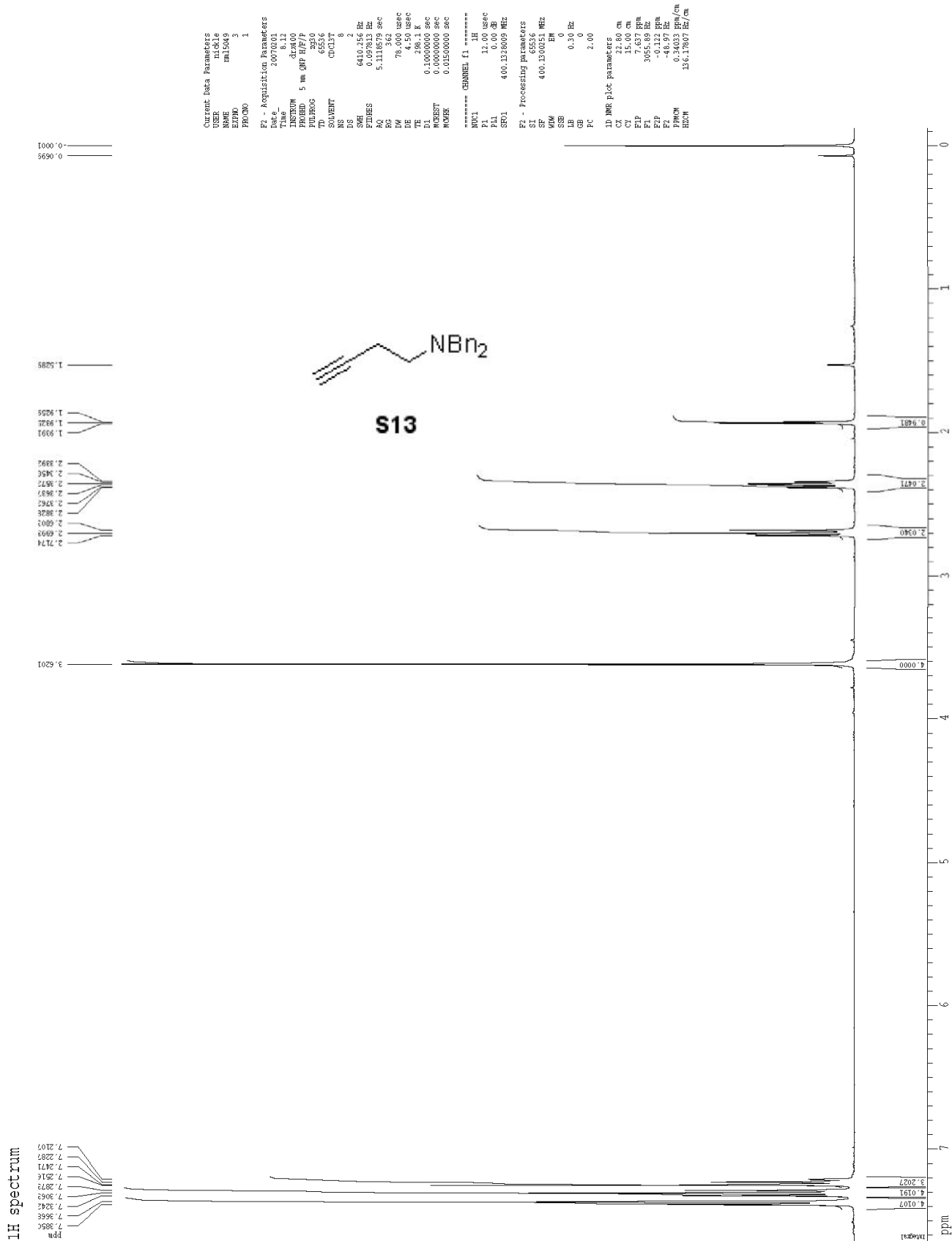


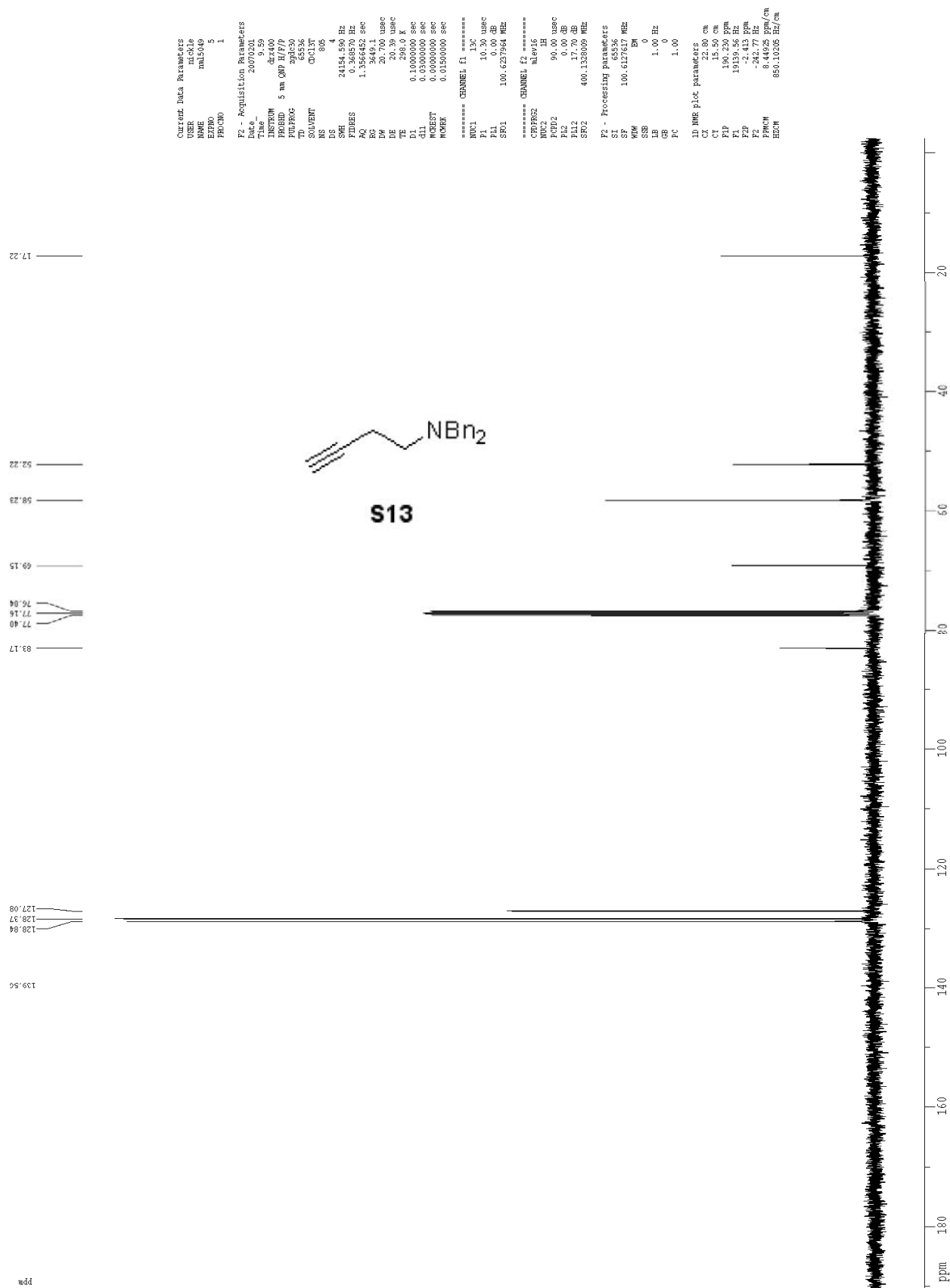
13C spectrum with 1H decoupling

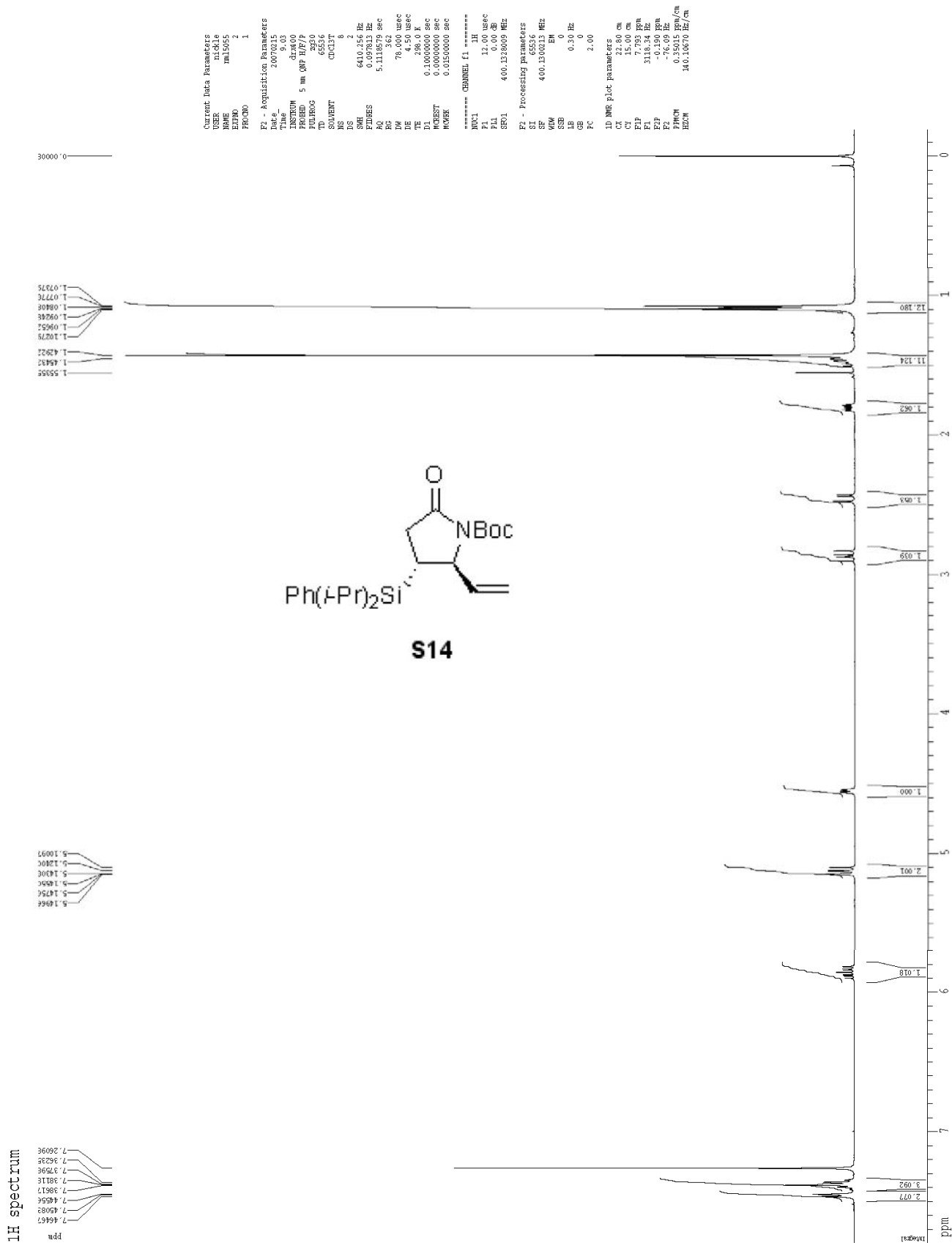


¹H spectrum

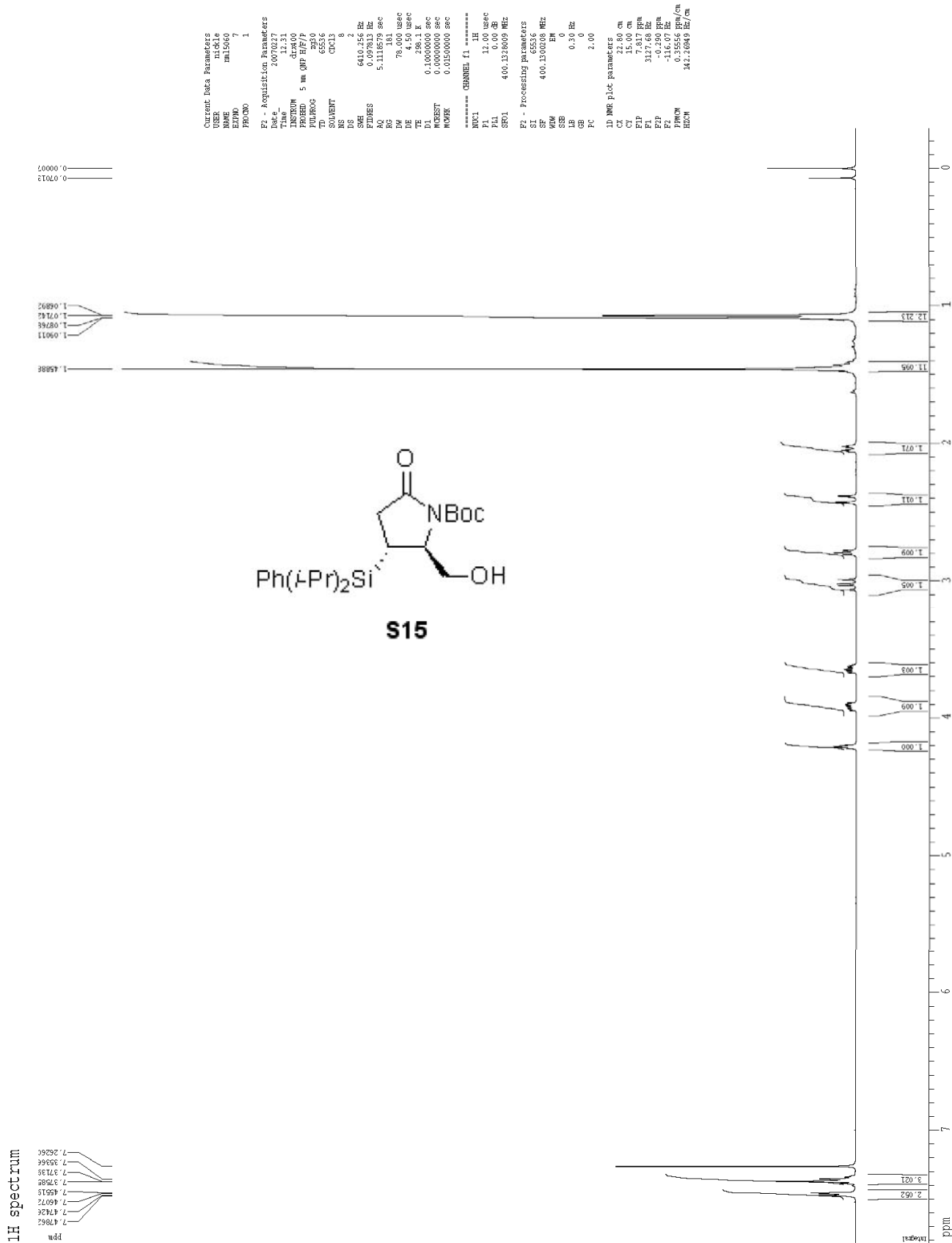
¹³C spectrum with ¹H decoupling

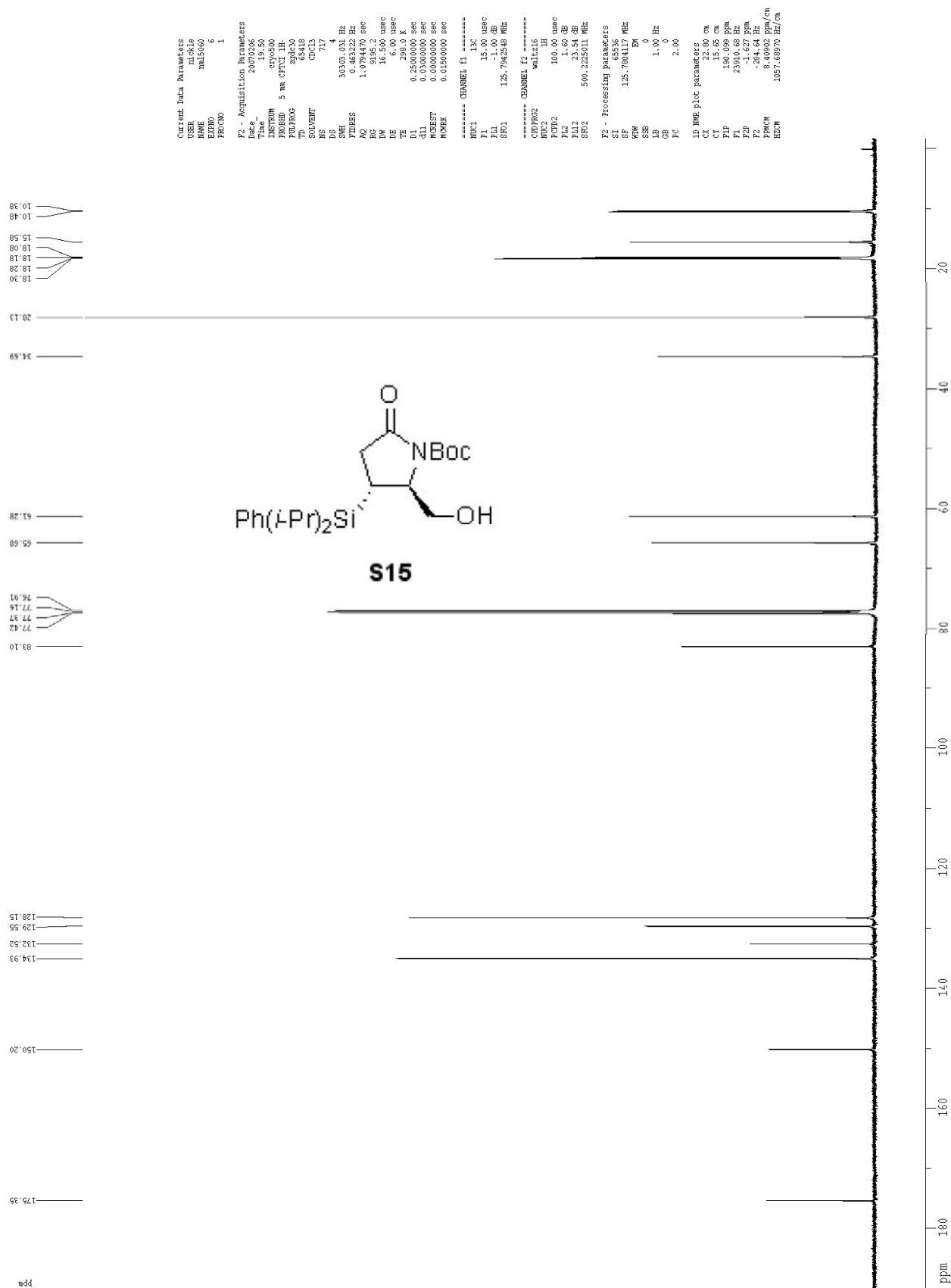


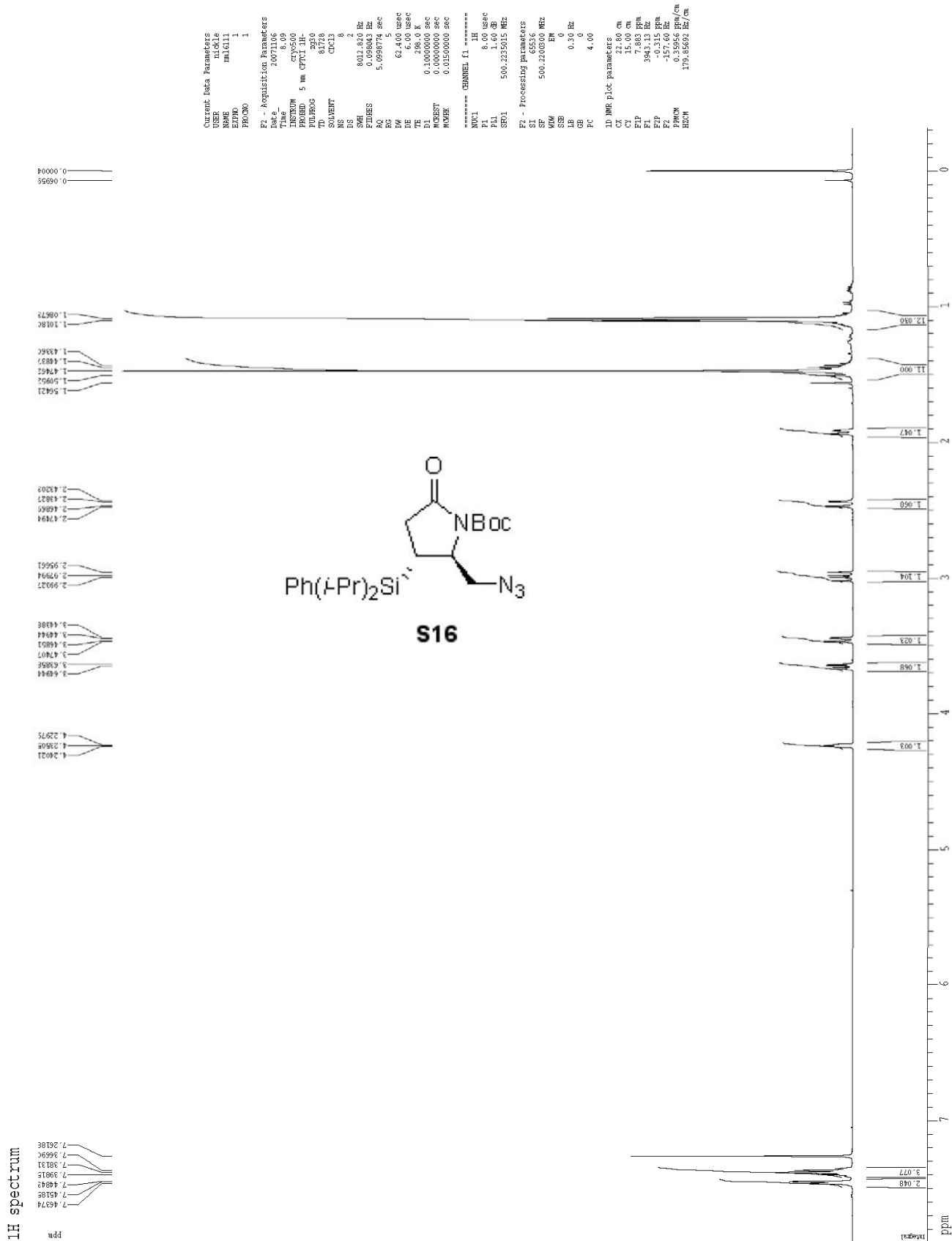
¹³C spectrum with ¹H decoupling

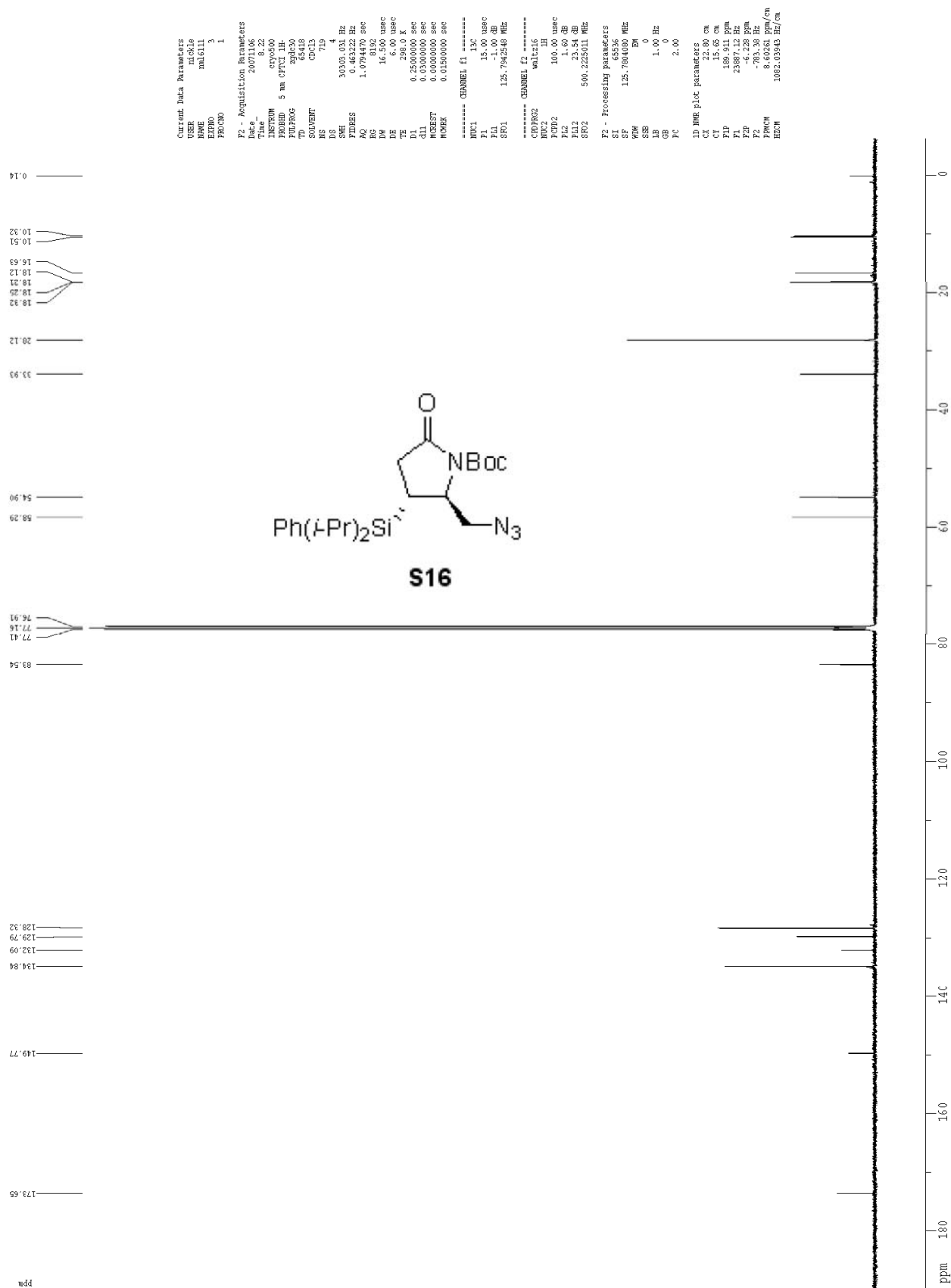


¹³C spectrum with ¹H decoupling

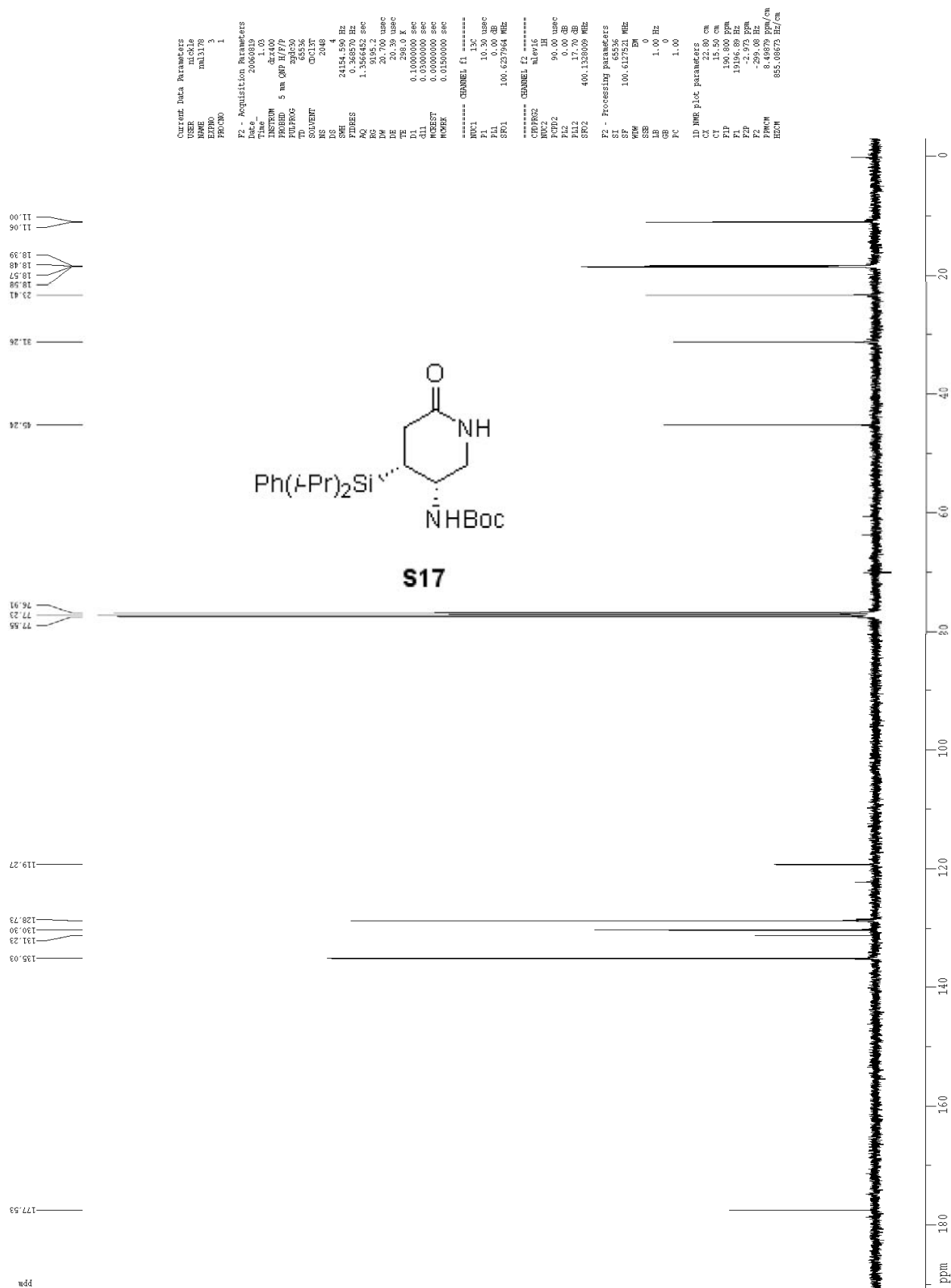


¹³C spectrum with ¹H decoupling

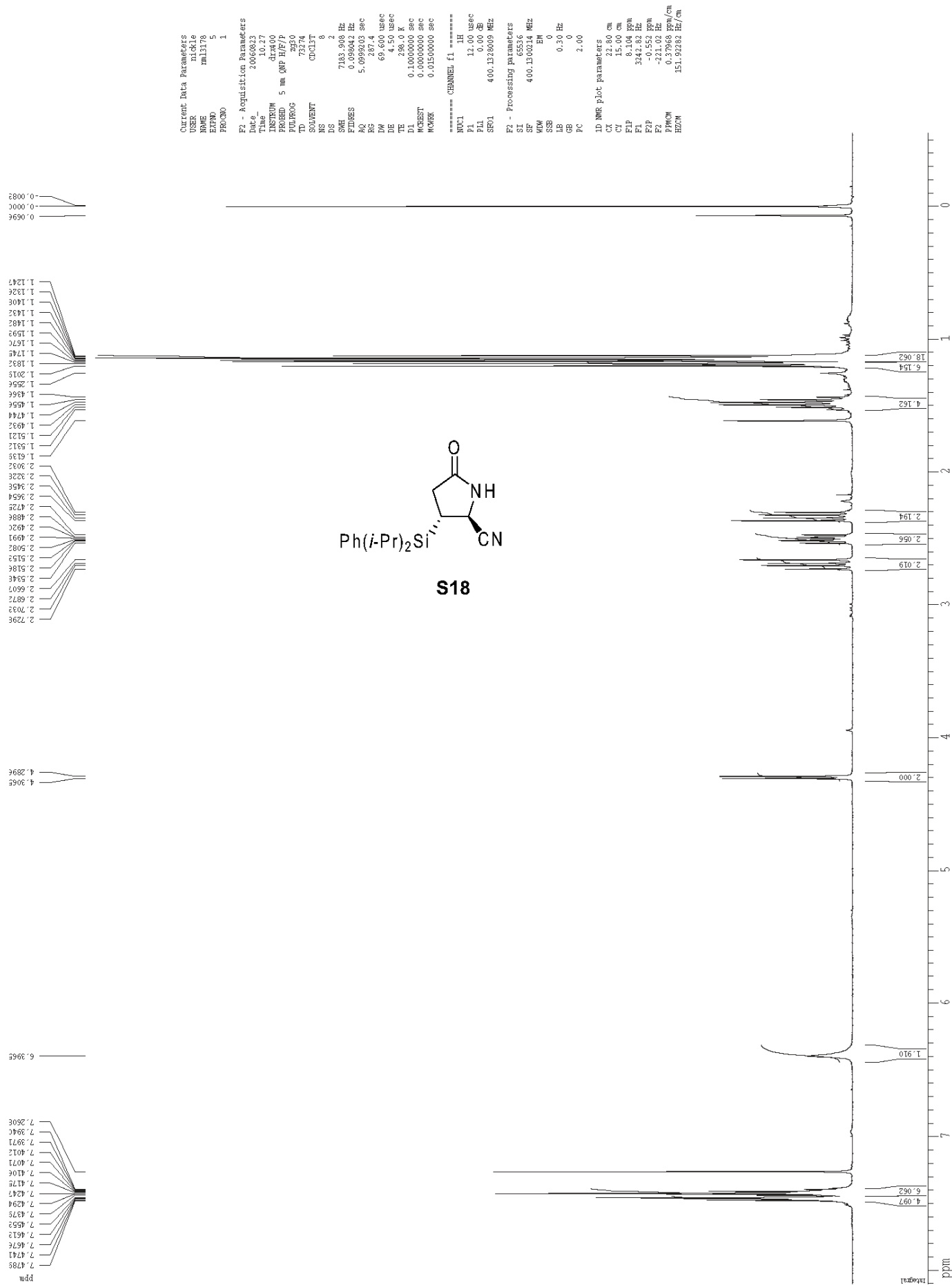


¹³C spectrum with ¹H decoupling

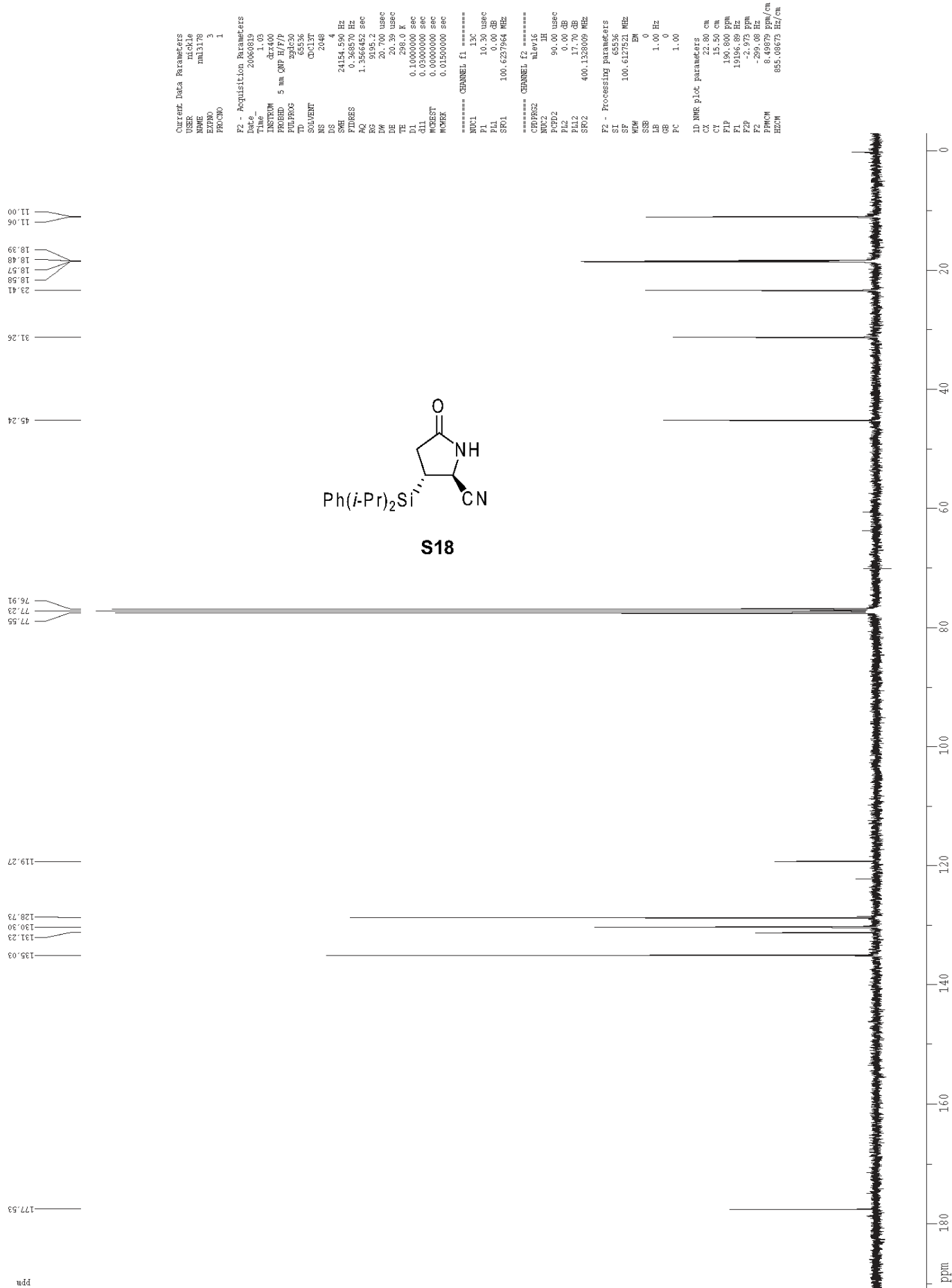
PI Woerpel
c13 CDCl3T v nickle 32

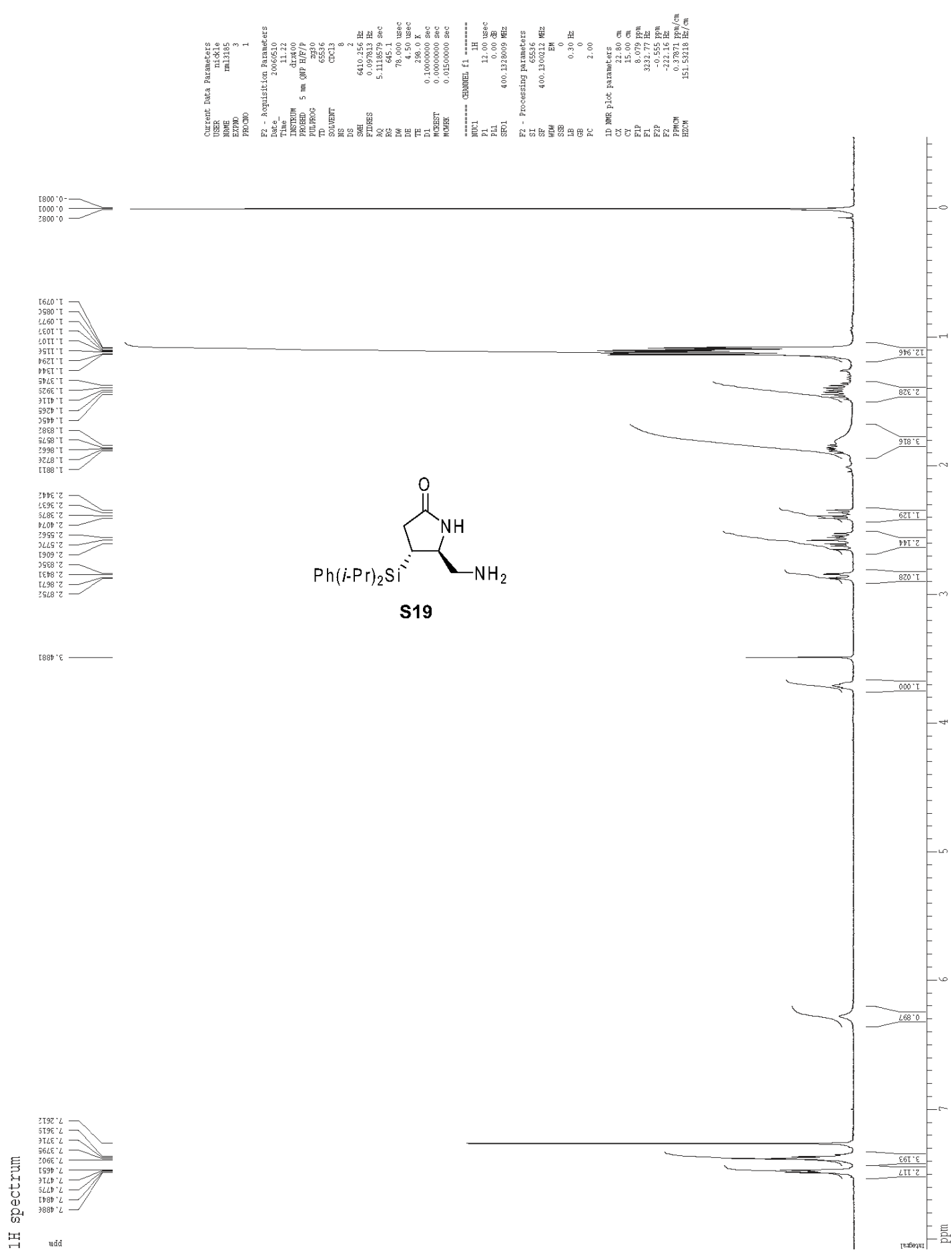


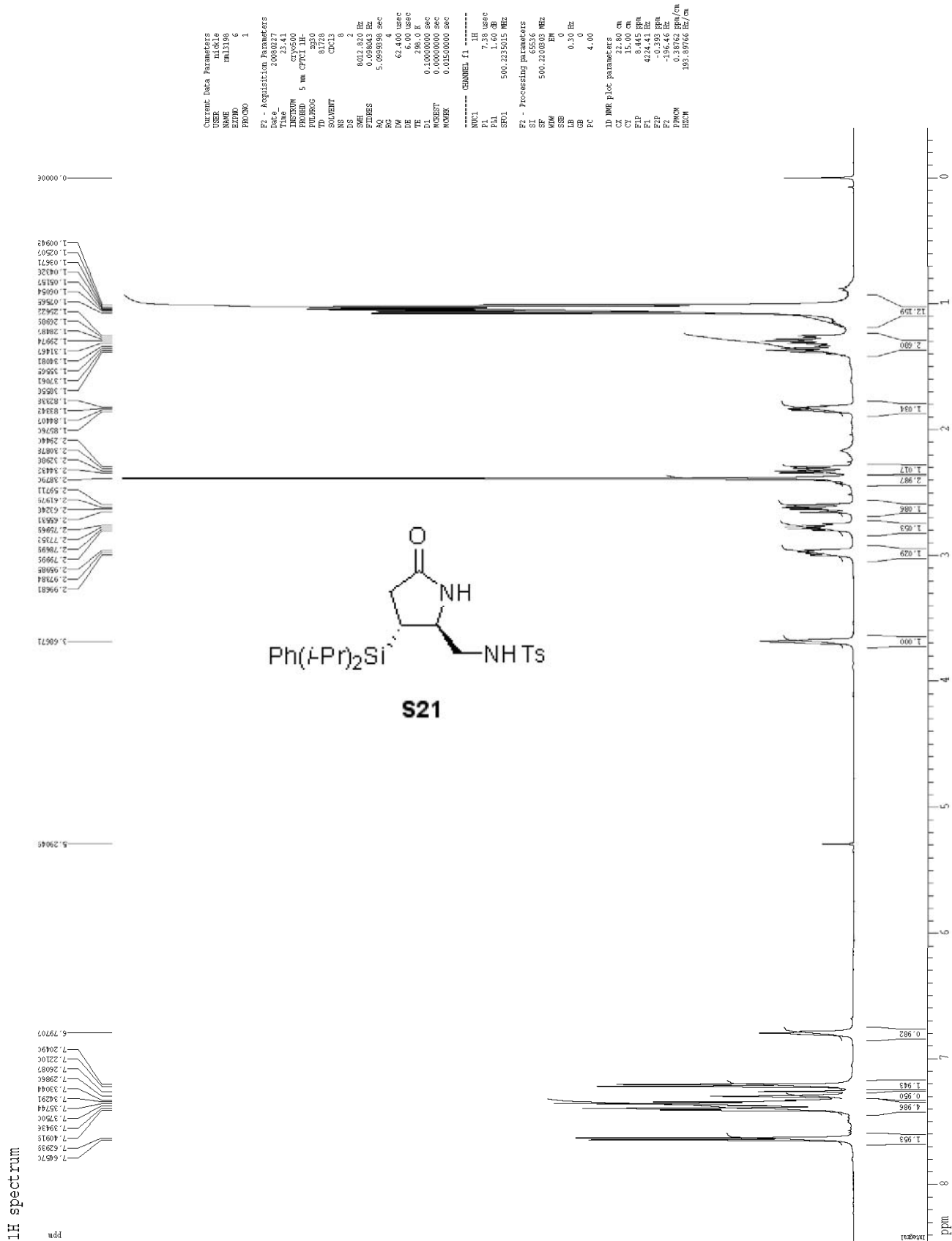
F1 Woerpel
h1 CDCl3 v nickle 53

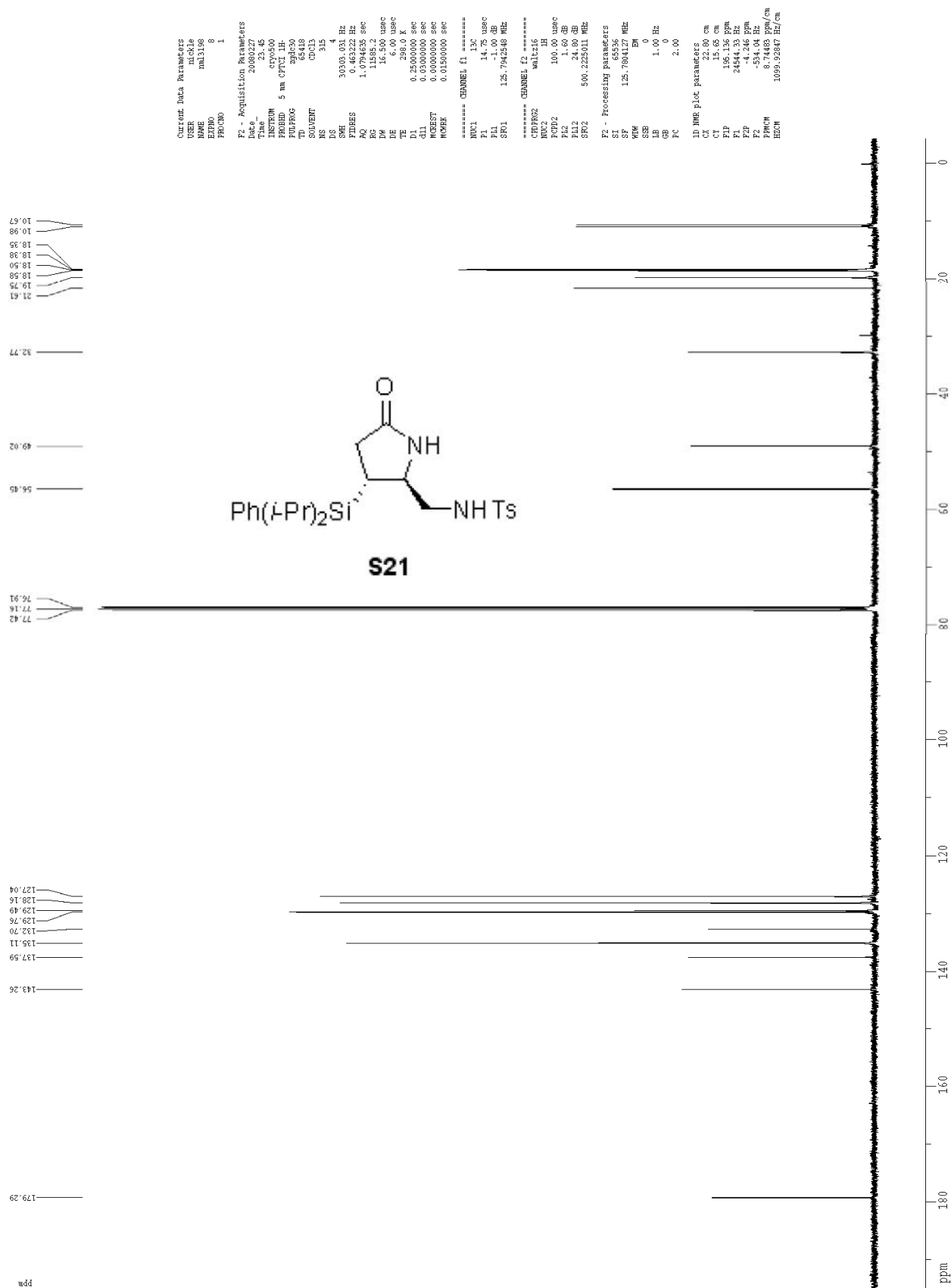


F1 Woerpel
c13 CDCl3T v nickle 32







¹³C spectrum with ¹H decoupling

¹H spectrum

ppm

7.47356
7.46097
7.45808
7.44466
7.43631
7.43206
7.41782
7.41434
7.26276

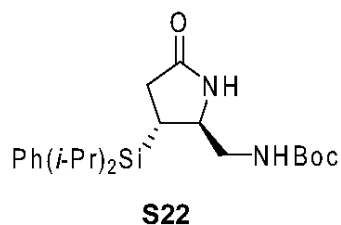
3.98800

2.67660
2.67041
2.65342
2.63925

2.04767

1.66914
1.50274
1.20435
1.18823
1.18601
1.18155
1.16987
1.16295
1.14740
1.12887

0.06956
0.00011



Current Data Parameters
 USER nickie
 NAME 1613192
 EXPNO 2
 PROCNO 1
 F2 - Acquisition Parameters
 Date_ 20060516
 Time 16.34
 INSTRUM dr400
 PROBRD 5 mm QNP H/P
 PULPROG zgpg30
 PC 65536
 SOLVENT CDCl3
 NS 8
 DS 2
 SWH 6410.256 Hz
 FIDRES 0.097813 Hz
 AQ 5.1118579 sec
 RG 574.7
 DW 78.000 usec
 DE 4.50 usec
 TE 300.2 K
 T1 0.10000000 sec
 T1RHO 0.00000000 sec
 MCHST 0.00000000 sec
 MCHKE 0.01500000 sec
 ===== CHANNEL f1 =====
 NUC1 1H
 P1 12.00 usec
 PL1 0.00 dB
 SFO1 400.1326009 MHz
 F2 - Processing parameters
 SI 65536
 SF 400.1300208 MHz
 WDM 0
 EM 0
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 2.00
 1D FID plot parameters
 CX 22.80 cm
 CY 15.00 cm
 F1F 8.697 ppm
 F1 3480.10 Hz
 F2F -0.509 ppm
 F2 -103.47 Hz
 FWHM 0.40377 ppm/cm
 HZM 161.56004 Hz/cm

Integral

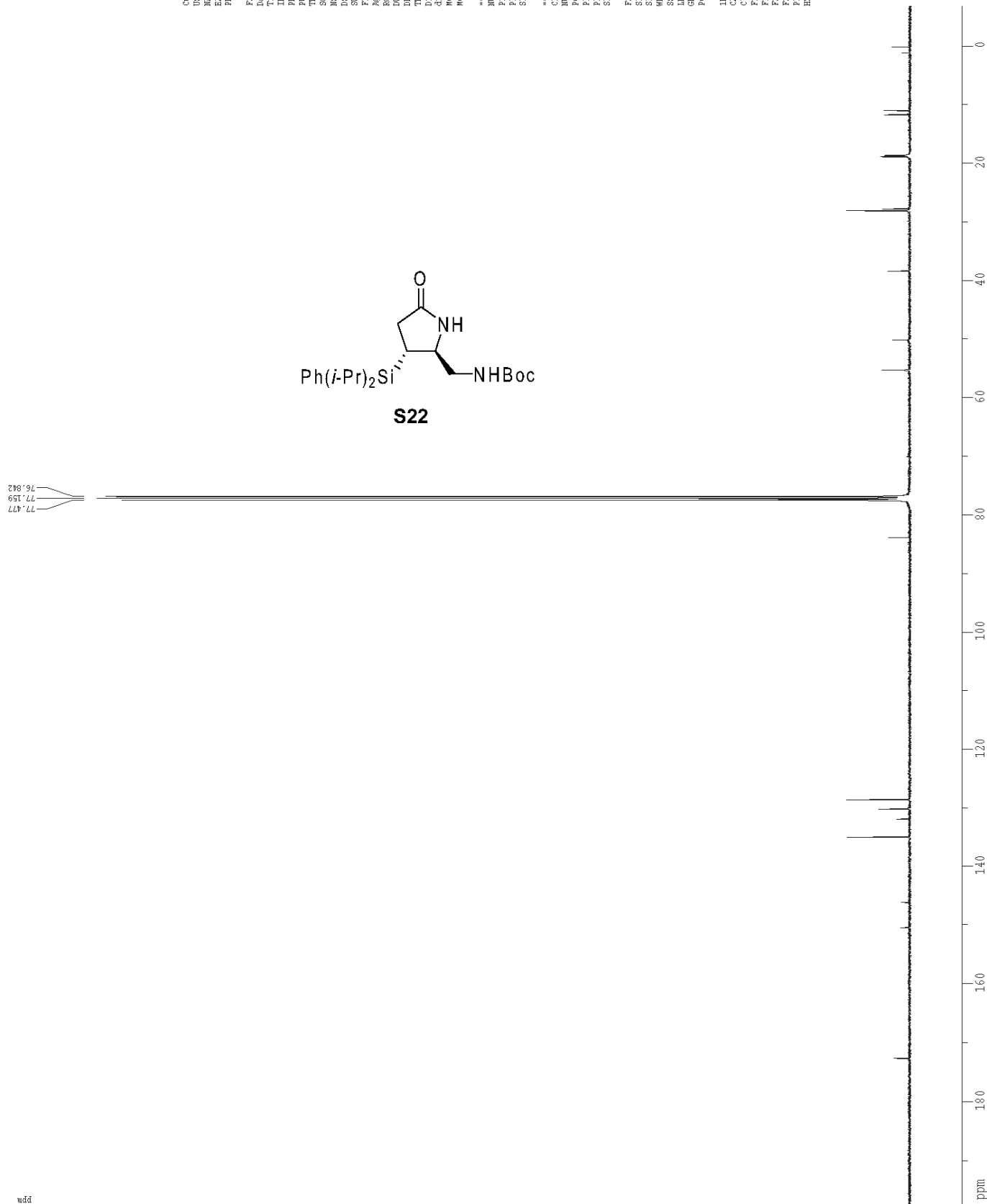
ppm

12.502
2.193
8.996
1.157
2.033
1.037
1.000
1.108

0
1
2
3
4
5
6
7
8

¹³C spectrum with ¹H decoupling

wdd



Current Data Parameters
 USER mckie
 NAME ml3192
 EXPNO 4
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20060531
 Time 8.07
 INSTRUM drx400
 PROBHD 5 mm QNP H/F/P
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 4
 DS 4
 SWH 24154.590 Hz
 FIDRES 0.368570 Hz
 AQ 1.35664452 sec
 RG 9195.2
 DW 20.700 usec
 DE 20.39 usec
 TE 297.9 K
 D1 0.10000000 sec
 d11 0.03000000 sec
 ACQRES 0.00000000 sec
 FWHM 0.01500000 sec

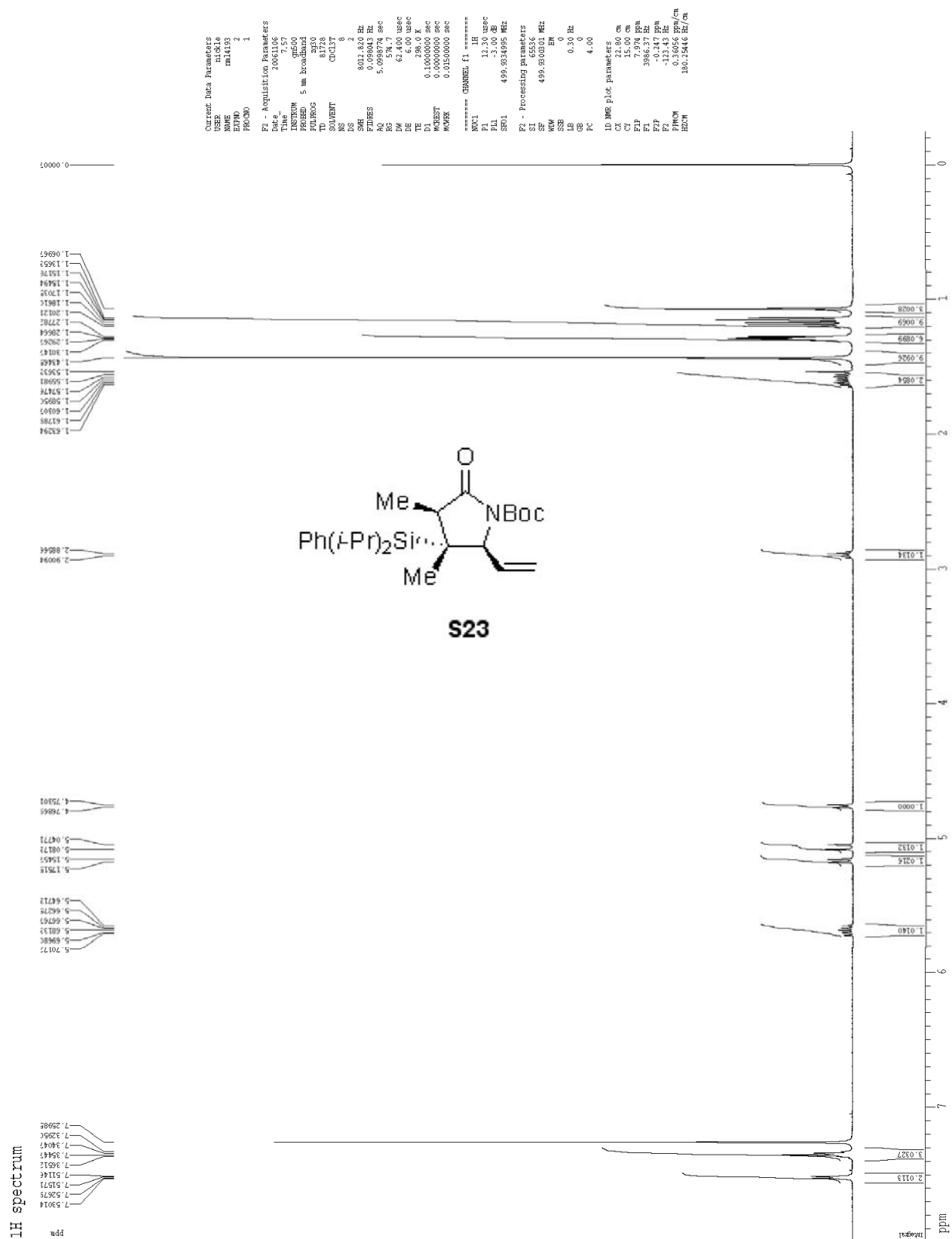
===== CHANNEL f1 =====
 NUC1 ¹³C
 P1 10.30 usec
 PL1 0.00 dB
 SFO1 100.6237964 MHz

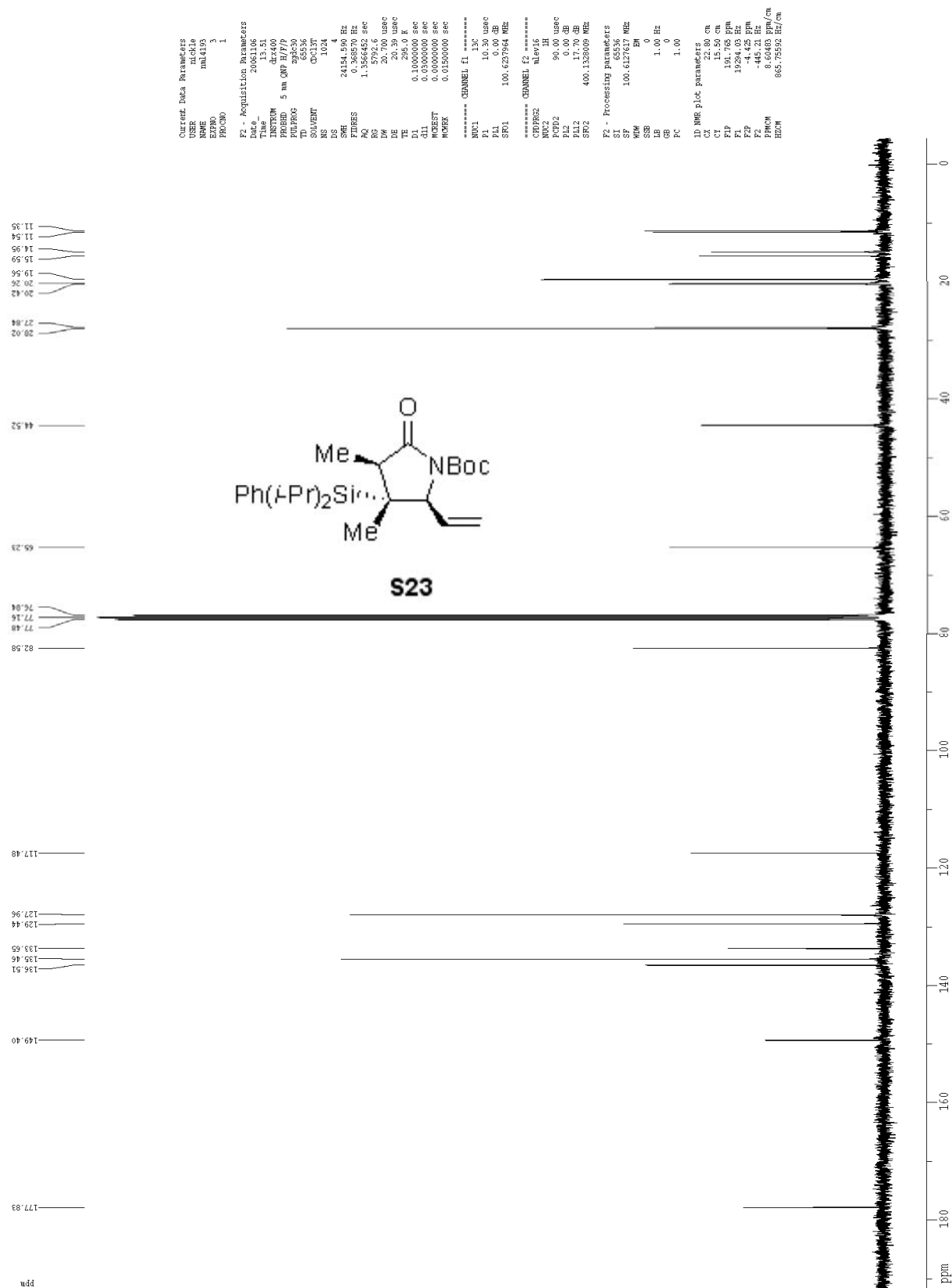
===== CHANNEL f2 =====
 CDPFG2 mlev16
 NUC2 ¹H
 P2 90.00 usec
 PL2 19.00 dB
 PL12 17.20 dB
 SFO2 400.1328099 MHz

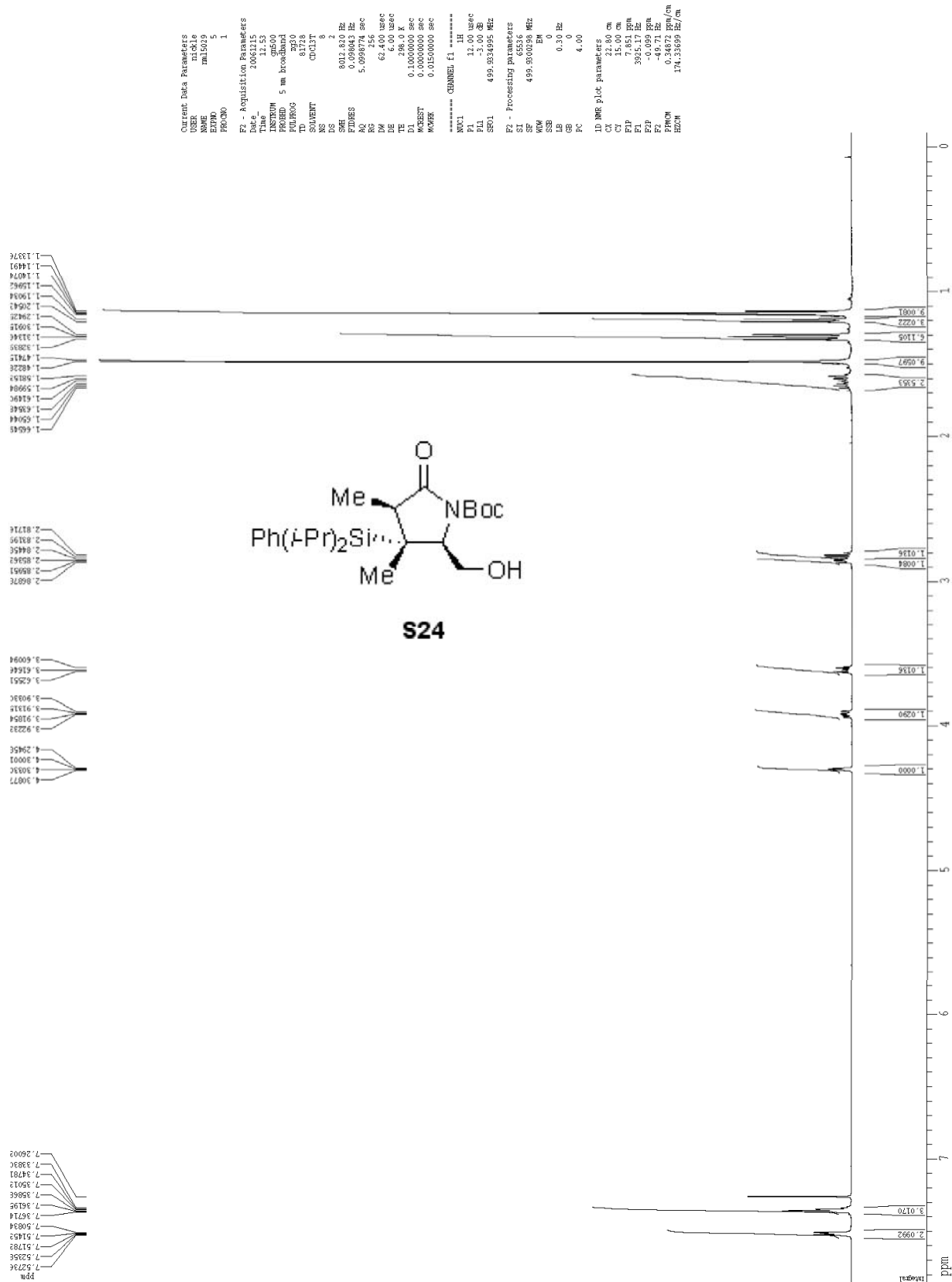
F2 - Processing parameters
 SI 65536
 SF 100.6127580 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.00

1D FINE plot parameters
 CX 22.80 cm
 CY 15.50 cm
 F1P 197.718 ppm
 F1 19882.95 Hz
 F2P -6.837 ppm
 F2 -687.91 Hz
 FPMCM 8.571172 ppm/cm
 HZCM 902.66937 Hz/cm

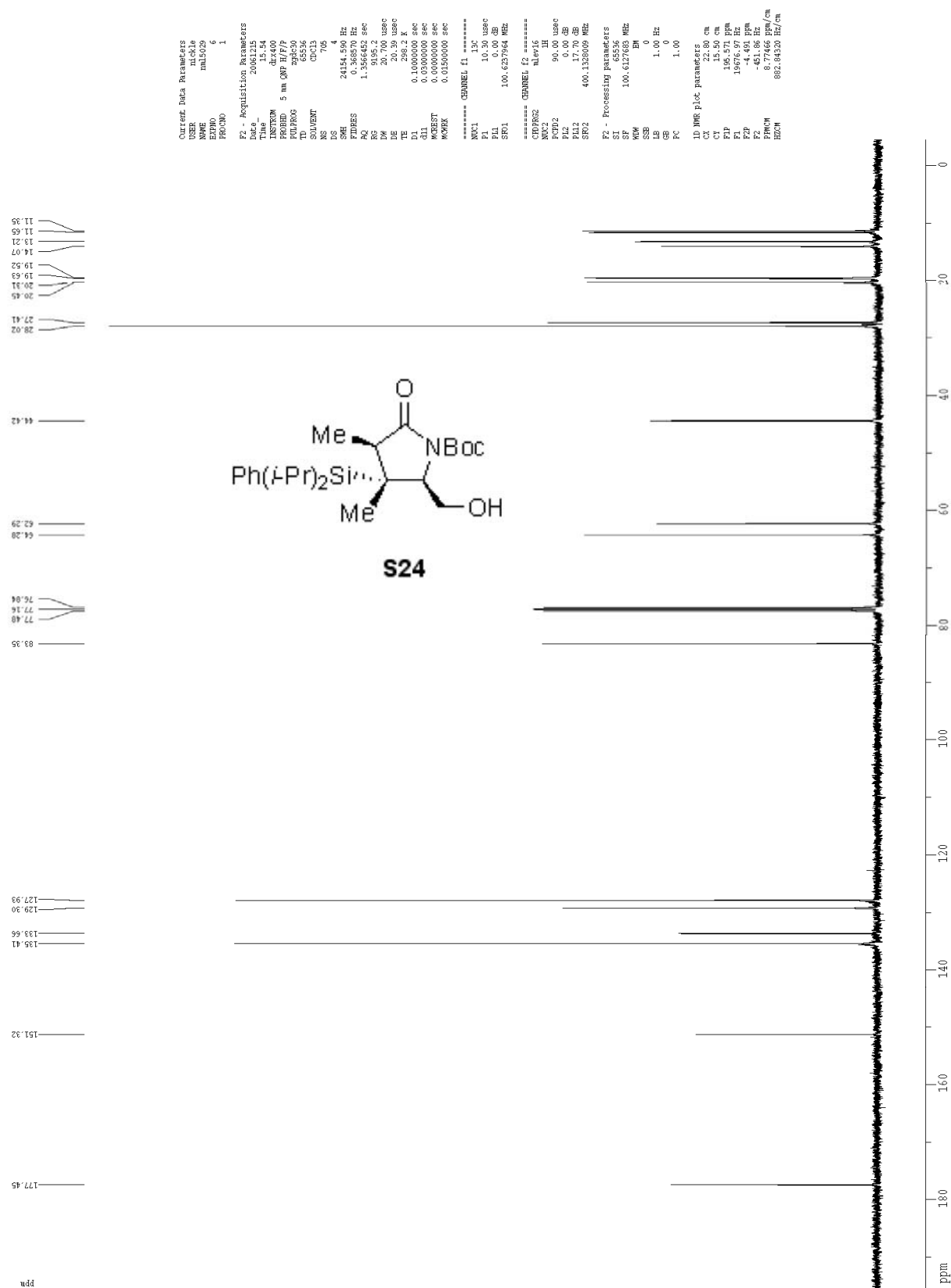
Note: Compound **S23** is an intermediate in the formation of azide **3** (Scheme 1.)



PI Woerpel
c13 CDC13T v nickle 10

¹H spectrum

¹³C spectrum with ¹H decoupling



¹H spectrum

Chemical structure of S25:

C[C@H]1C(=O)N(Cc2ccccc2)[C@@H](C)[C@H]1COP(=O)(OC)c3ccccc3

S25

Current Data Parameters
USER nickle
NAME ml5007
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20080113
Time 8.33
INSTRUM spect
PROBHD 5 mm QNP H/F/7
PULPROG zgpg30
TD 65536
SOLVENT cdcl3f
NS 8
DS 2
SWH 6410.245 Hz
FIDRES 0.097813 Hz
AQ 5.1118579 sec
RG 327.4
RW 78.00 MHz
DE 4.50 MHz
TE 298.1 K
D1 0.1000000 sec
d11 0.0500000 sec
DELTA 0.0500000 sec
MOVER 0.0150000 sec

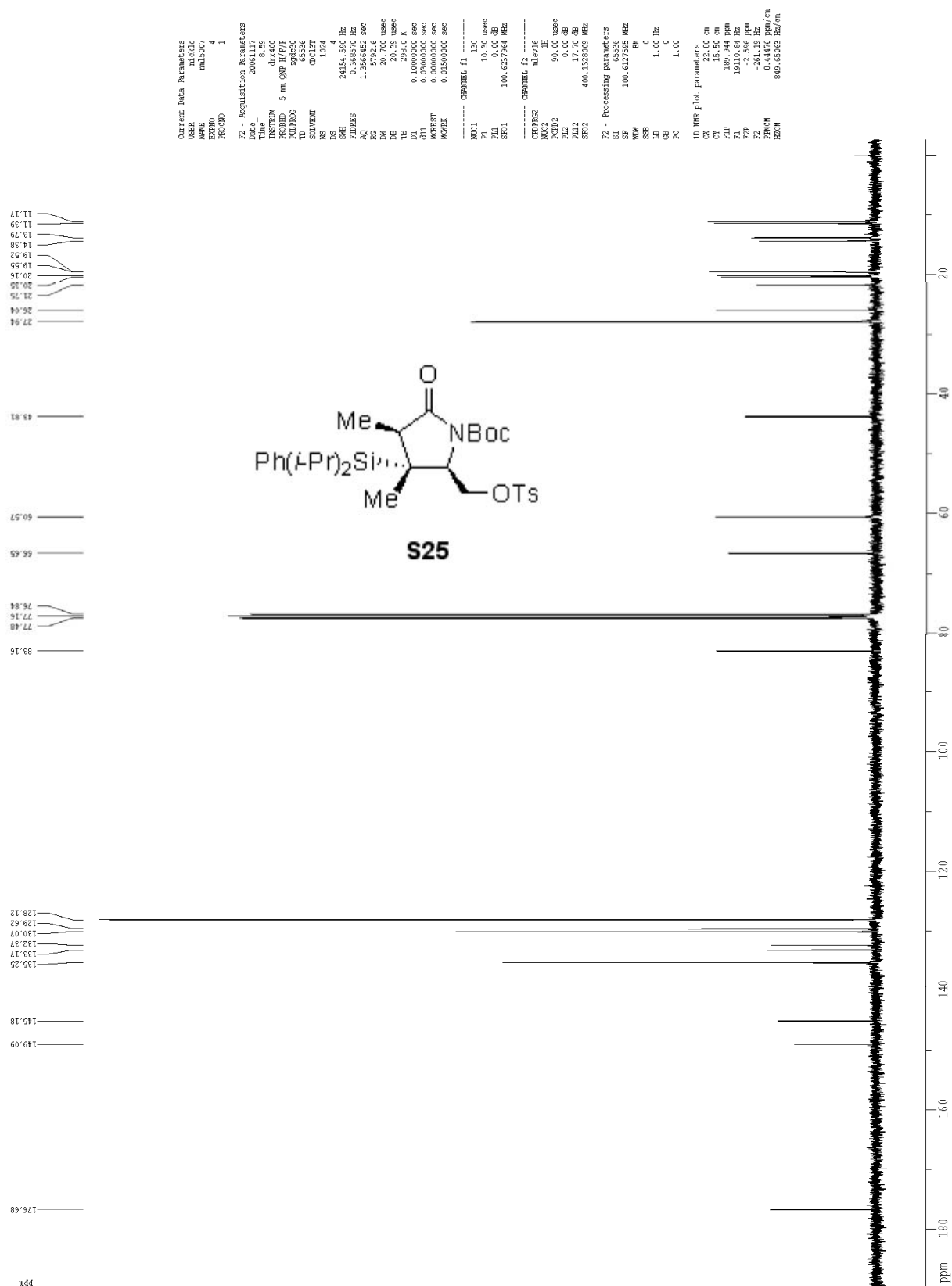
===== CHANNEL f1 =====
NUC1 13C
P1 12.00 usec
PL1 0.00 dB
SR01 400.1328009 MHz

F2 - Processing parameters
SI 65536
SF 400.1300213 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 2.00

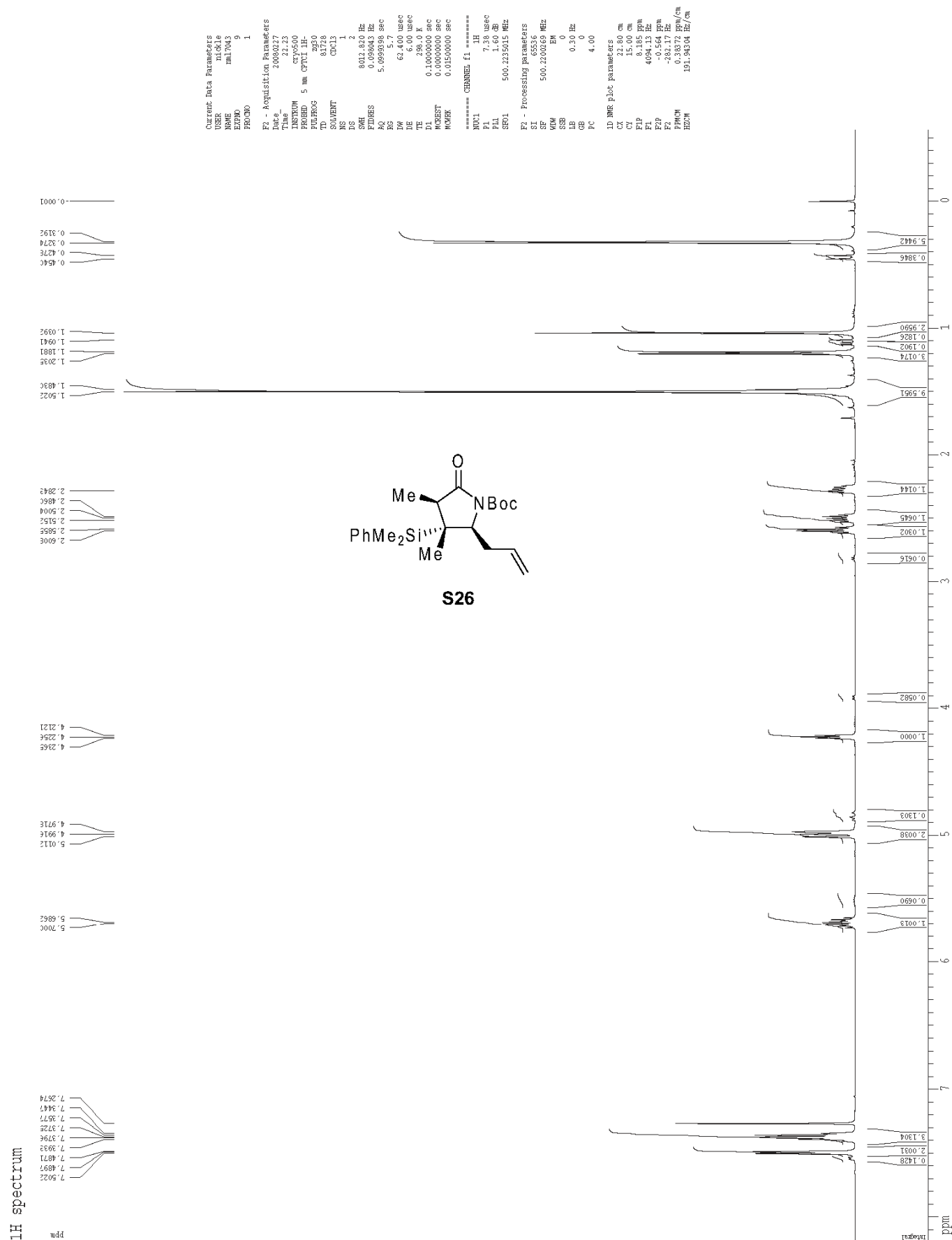
ID RMS plot parameters
CX 22.80 cm
CY 15.00 cm
FLIP 15.00 cm
F1P 3282.34 Hz
F2P -0.315 PPM
FZ -126.01 Hz
GAMMA 0.728356/cm
HZMM 149.48885 Hz/cm

Integration values (from left to right): 0.0075, 0.0001, 1.5507, 1.5454, 1.2975, 1.2388, 1.2195, 1.1796, 1.1691, 1.1608, 1.1501, 1.0964, 2.4164, 2.9116, 4.4315, 4.4154, 4.0072, 1.0000, 1.0034, 1.0009, 2.0032, 2.0094, 5.0093.

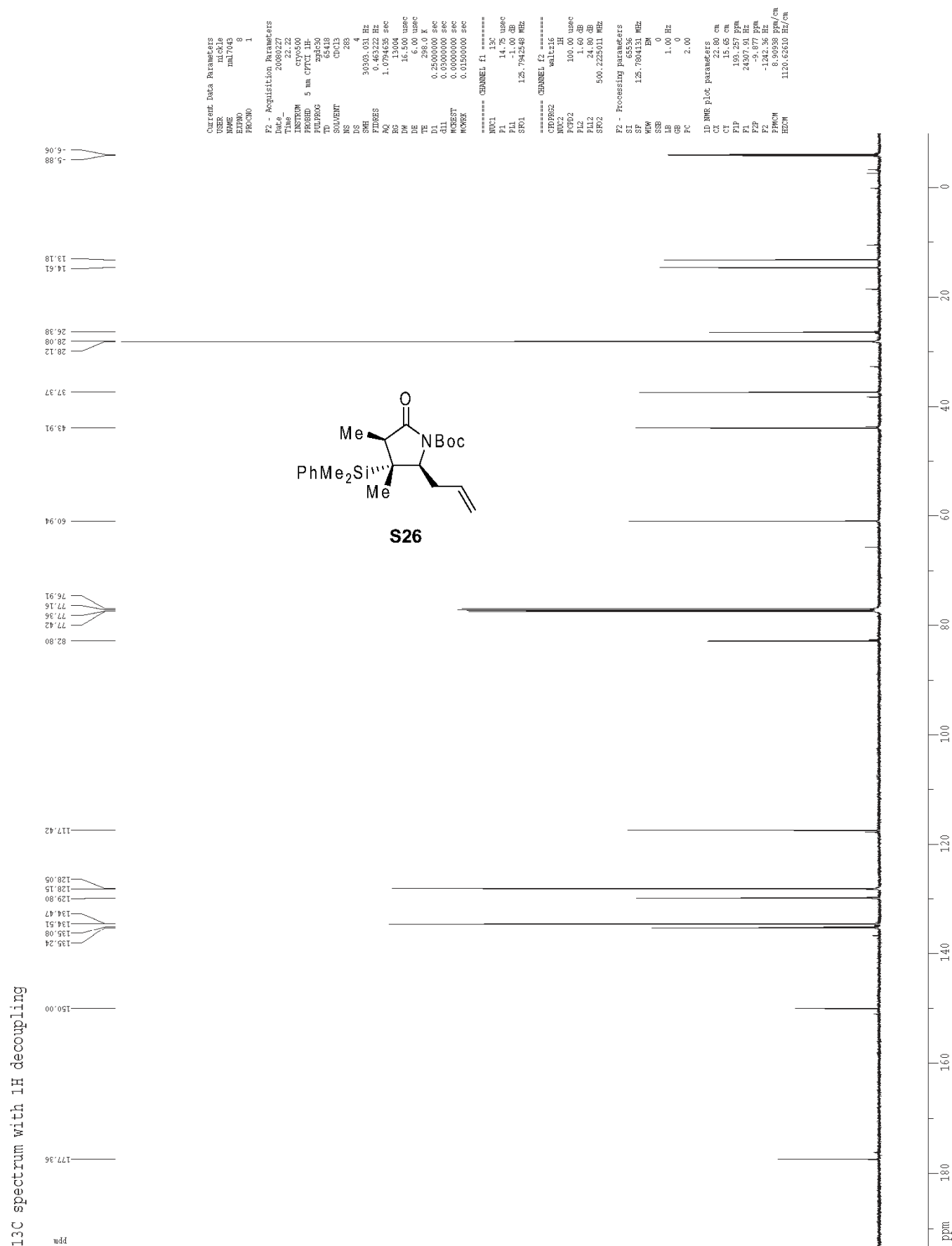
^{13}C spectrum with ^1H decoupling



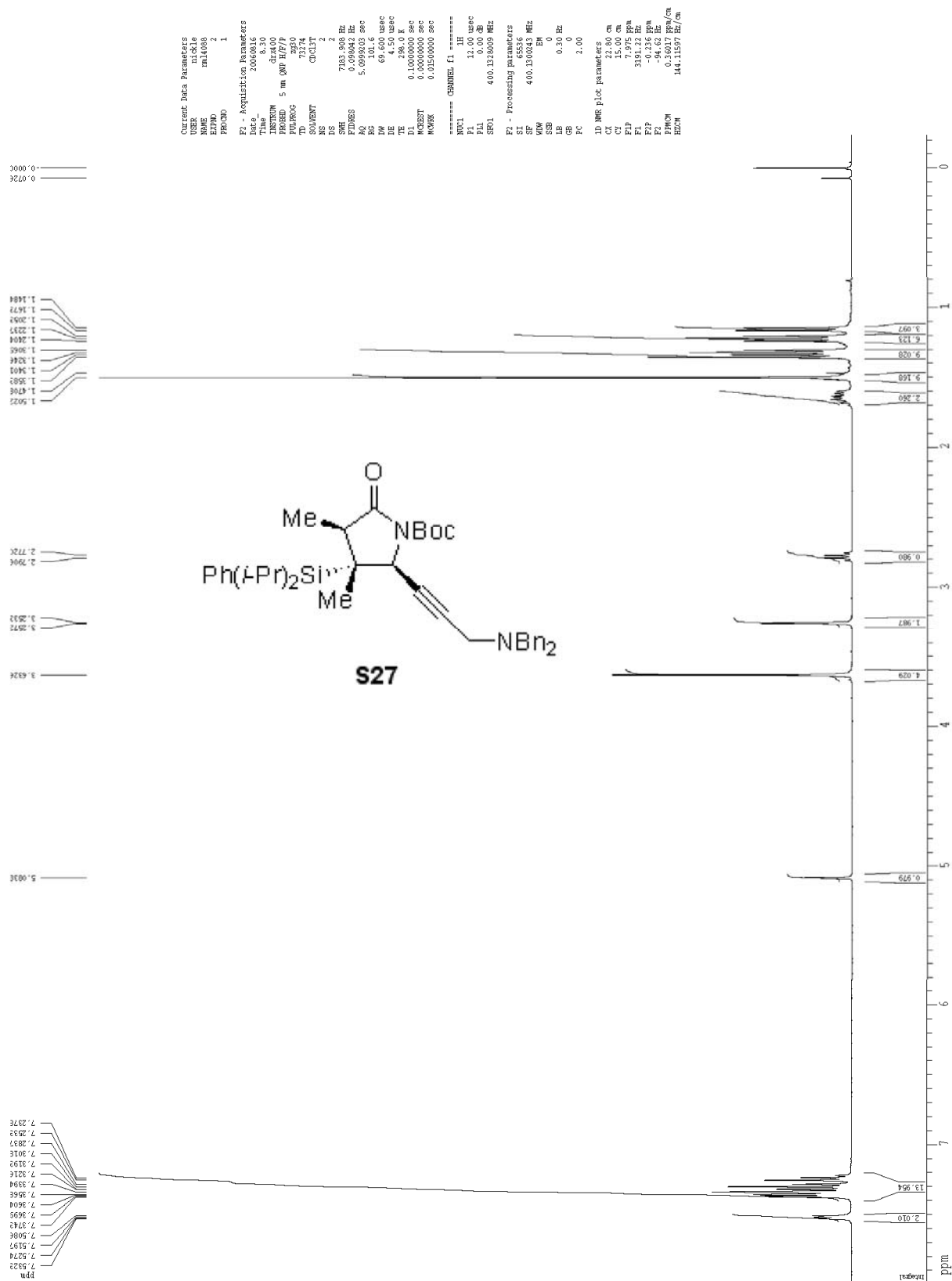
Note: Compound **S26** is an intermediate in the formation of lactam **18** (Scheme 3.)



Note: Compound **S26** is an intermediate in the formation of lactam **18** (Scheme 3.)

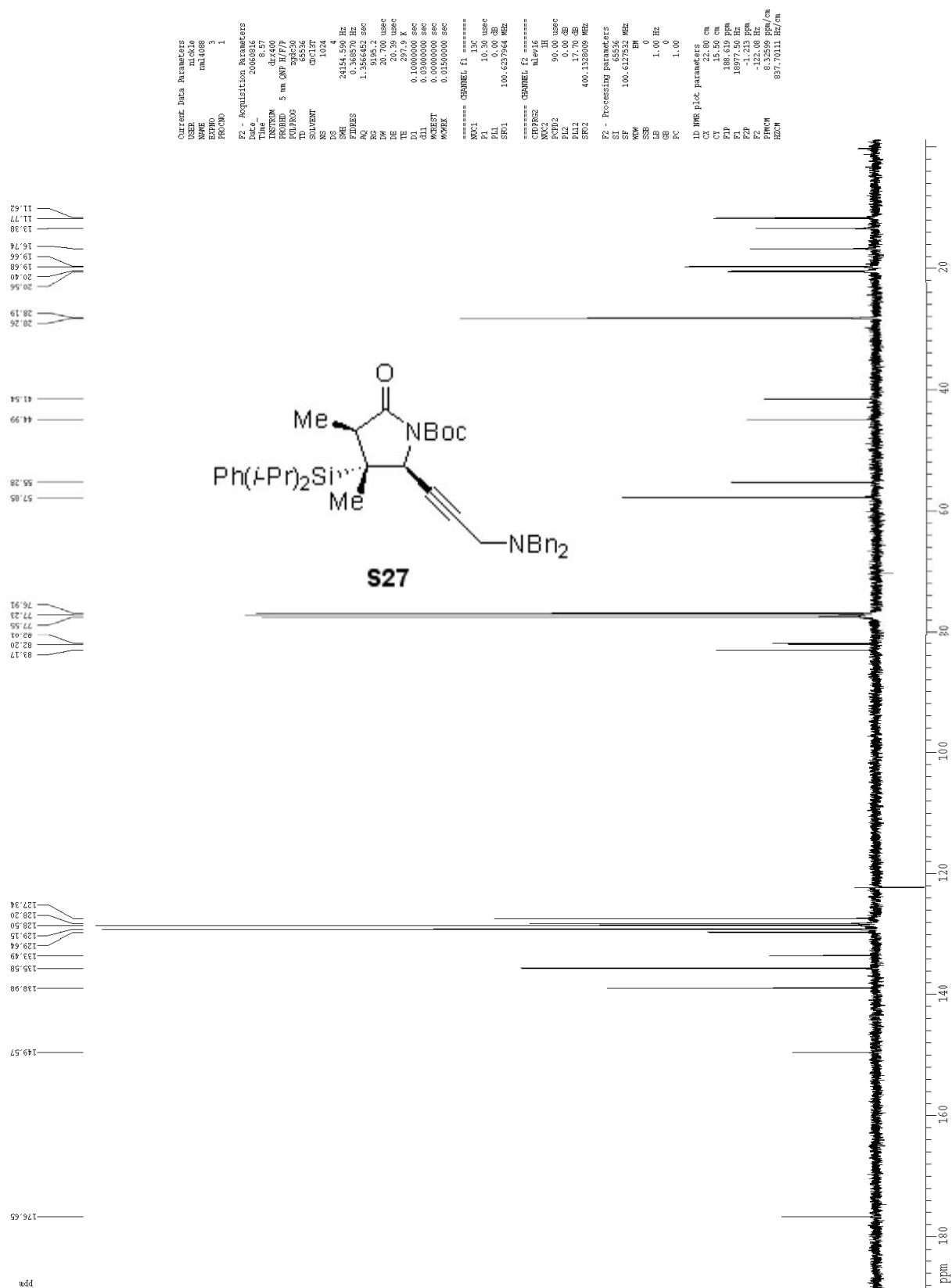


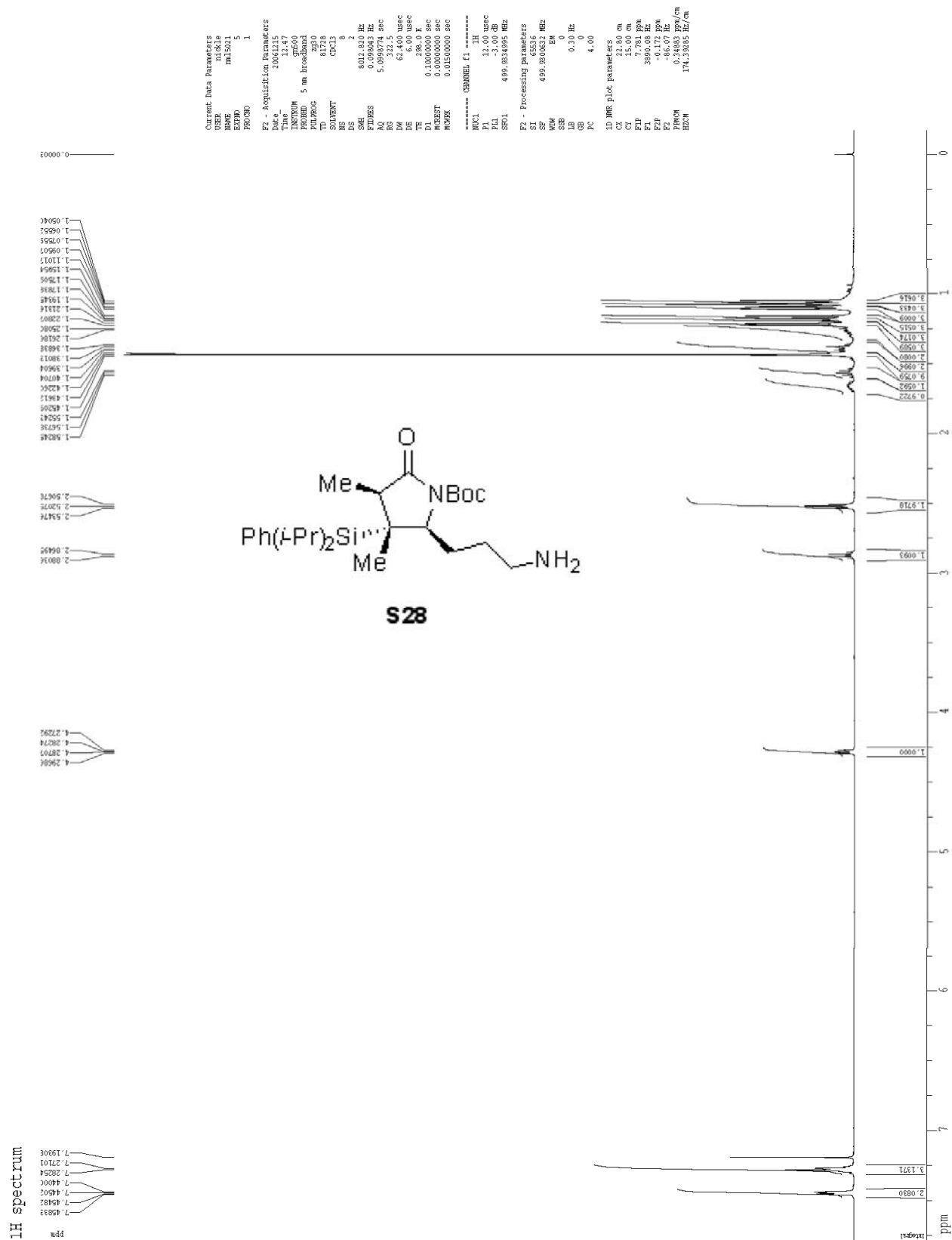
PI Woerpel
h1 CDCl3T v nickle 15



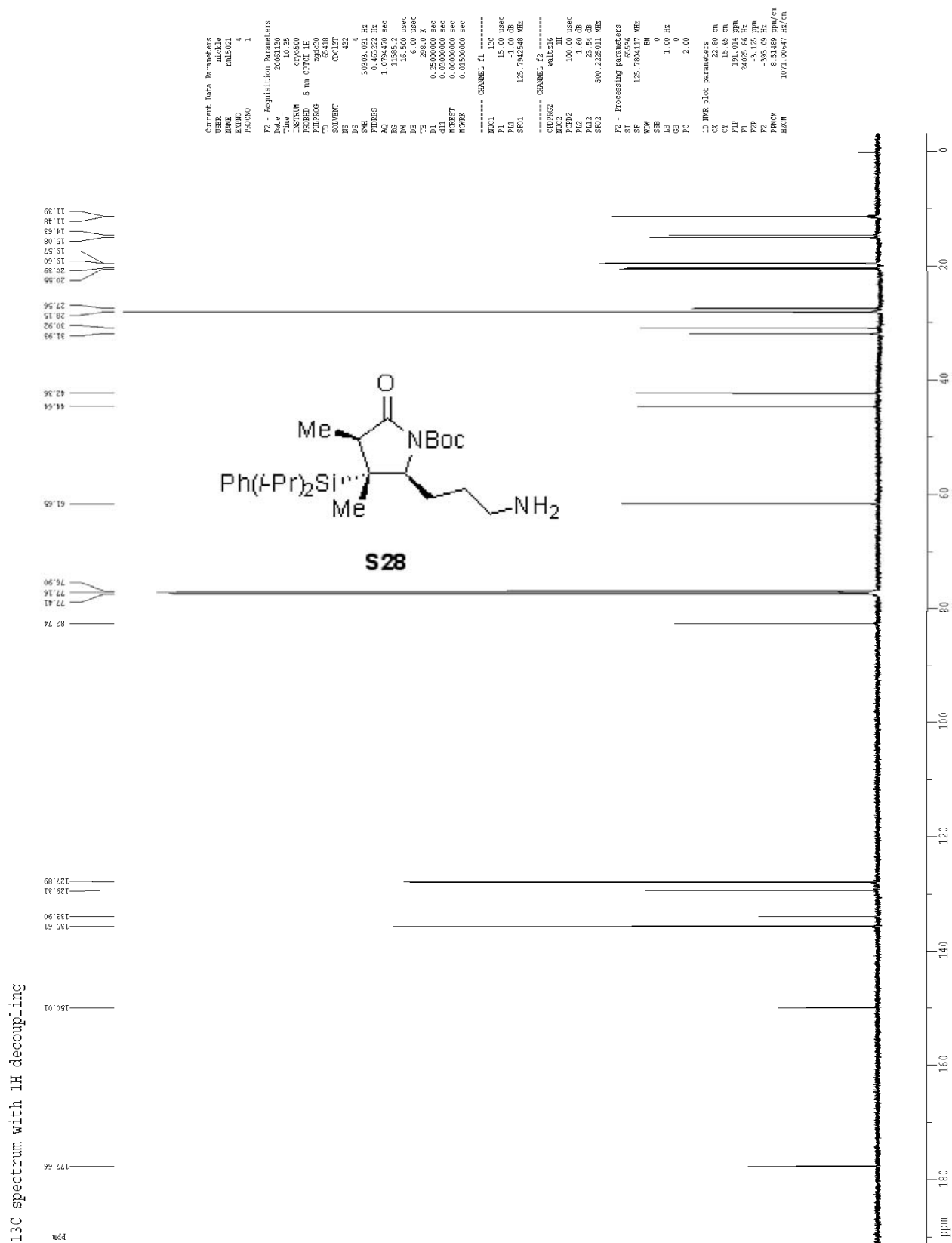
Note: Compound **S27** is an intermediate in the formation of lactam **19** (Scheme 4.)

PI Woerpel
c13 CDCl3T v nickle 15

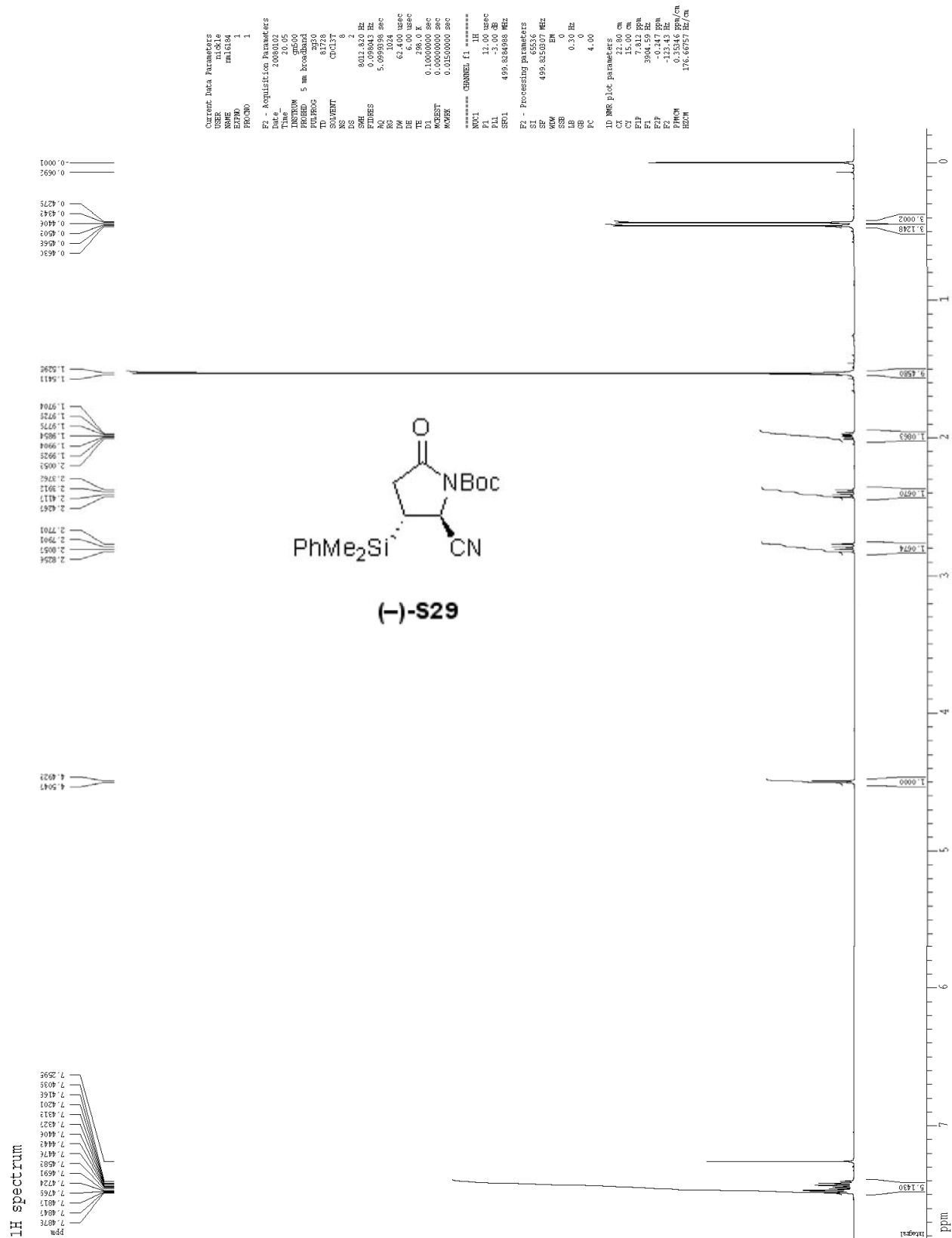


¹H spectrum

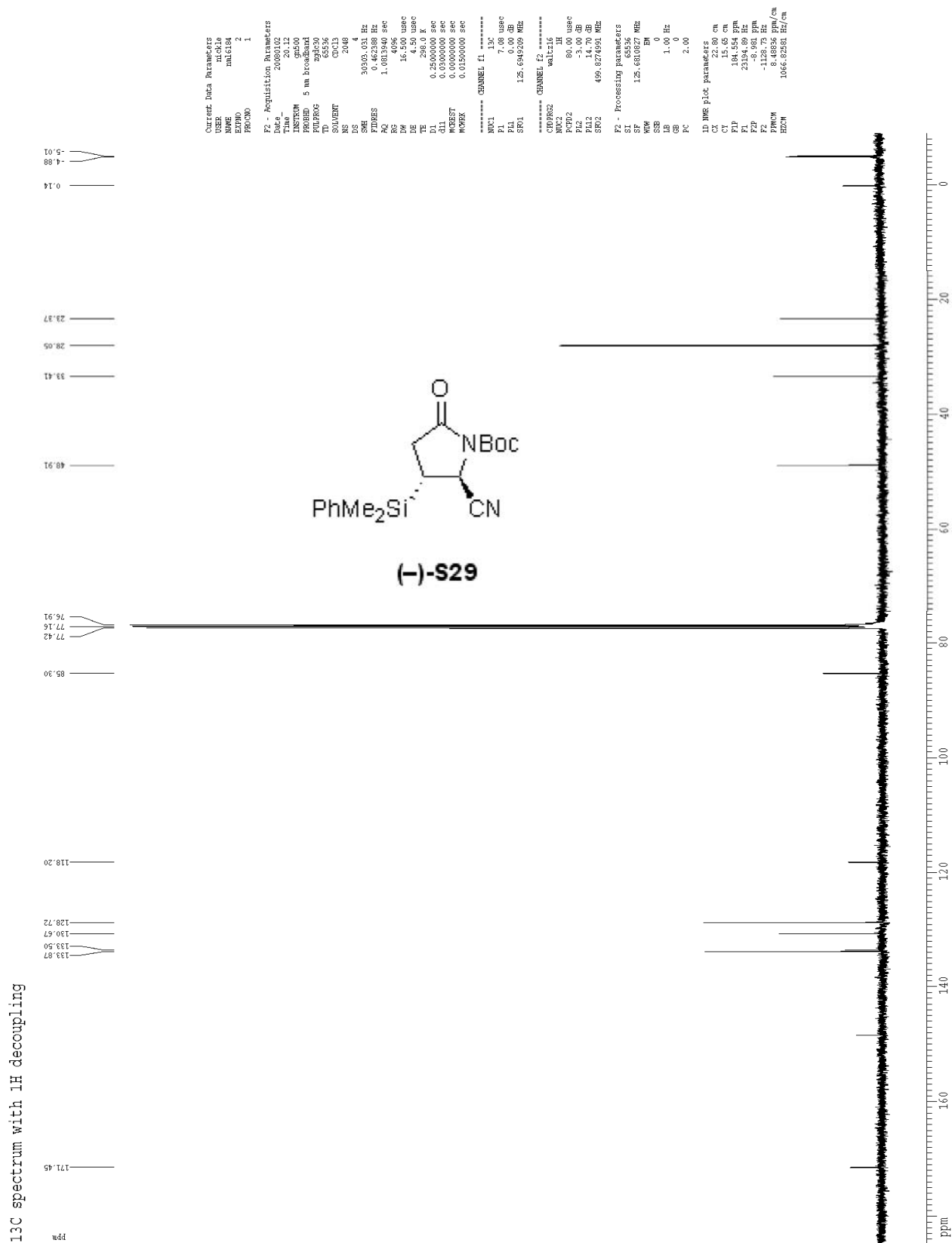
Note: Compound **S28** is an intermediate in the formation of lactam **19** (Scheme 4.)



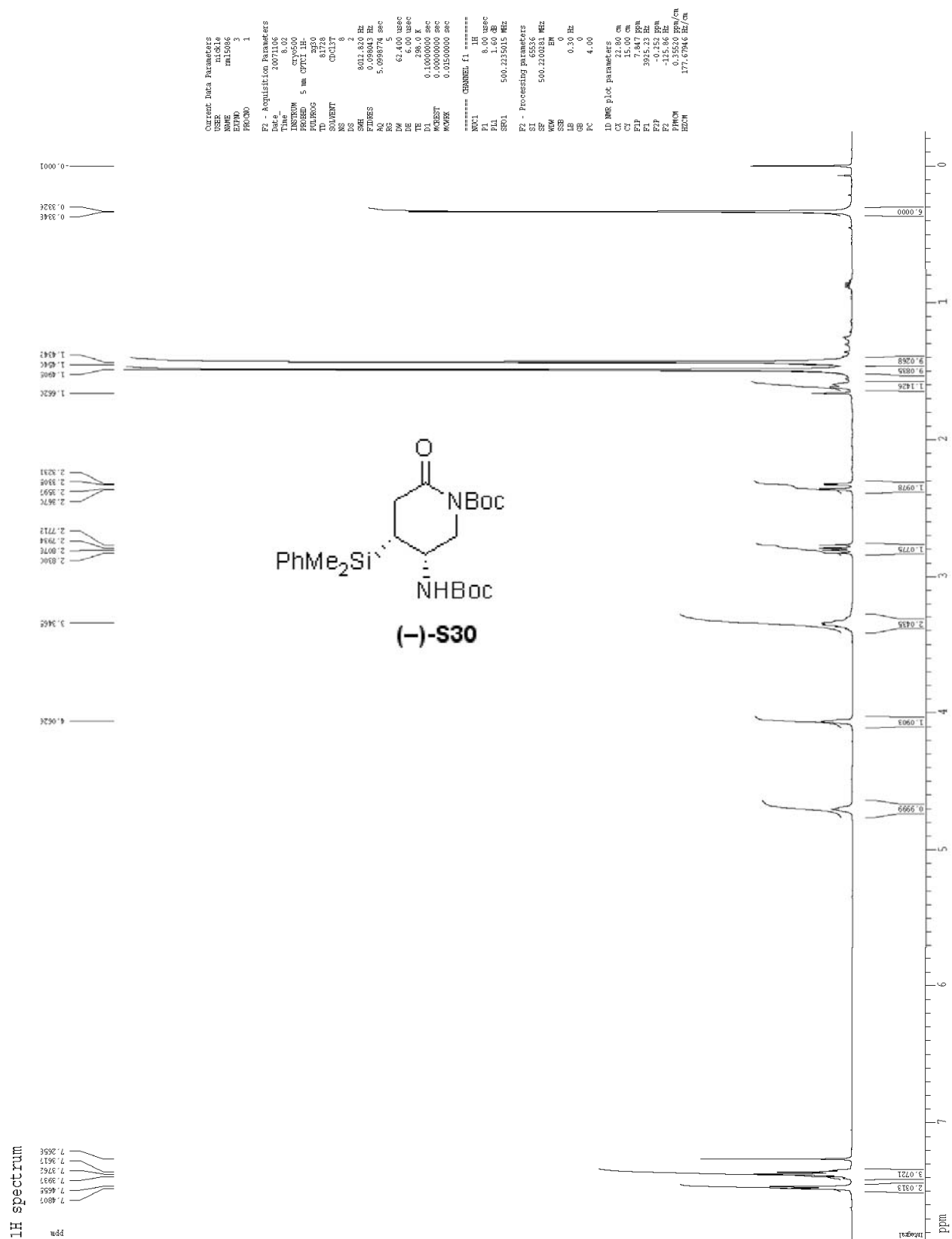
Note: Compound **(-)-S29** is an intermediate in the formation of *N,O*-acetal **(+)-21** (Scheme 5.)



Note: Compound (-)-**S29** is an intermediate in the formation of *N,O*-acetal (+)-**21** (Scheme 5.)



Note: Compound **(-)-S30** is an intermediate in the formation of *N,O*-acetal **(+)-21** (Scheme 5.)



Note: Compound (–)-**S30** is an intermediate in the formation of *N,O*-acetal (+)-**21** (Scheme 5.)

