

**Stereocontrolled Microwave-Assisted Domino [3,3]-Sigmatropic
Reactions: A Winstein-Overman Rearrangement for the
Formation of Differentiated Contiguous C–N Bonds**

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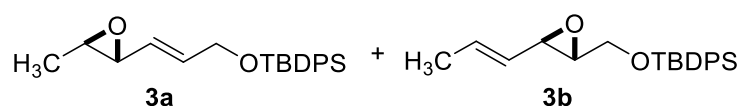
General Experimental:

Solvents were distilled fresh under nitrogen atmosphere before use and transferred via syringe using standard techniques unless otherwise stated. THF was dried over sodium and benzophenone before use. Dichloromethane was dried over calcium hydride before use. All reagents were purchased from Aldrich, VWR or Fischer Scientific Ltd. and used as received unless otherwise stated. NMR solvent (CDCl_3 with and without TMS internal standard, CD_3OD) were purchased from Cambridge Isotopes Lab Inc. and used as received. All products were characterized by ^1H NMR and ^{13}C NMR, IR, HRMS. ^1H NMR and ^{13}C NMR were recorded on Varian Mercury 300, 400 MHz, Bruker 400 MHz spectrometers. Chemical shifts are expressed in ppm values. ^1H NMR chemical shifts were internally referenced to the solvent resonance (δ 7.26 for CDCl_3 , δ 3.31 for CD_3OD). ^{13}C NMR chemical shifts were internally referenced to the solvent resonance (δ 77.16 for CDCl_3 , δ 49.00 for CD_3OD). Peak multiplicities are designated by the following abbreviations: s, singlet; br.s, broad singlet; d, doublet; t, triplet; q, quartet; m, multiplet; J, coupling constant in Hz. The coupling constant J (Hz) has been rounded to 0.5 Hz for all compounds. If a coupling pattern can be assigned as a combination of multiplicities, then the listed abbreviations are combined to provide an appropriate descriptor for the observed patterns (i.e., dt - doublet of triplets). IR spectra were obtained on Perkin Elmer Spectrum 100 FT-IR Spectrometer with samples loaded as thin films with CH_2Cl_2 . Mass spectra were obtained by the University of Toronto mass spectral facility (AIMS); high resolution mass spectra (HRMS) were recorded on an Agilent 6538 UHD spectrometer (EI) or JEOL AccuTOF model JMS-T1000LC (DART-TOF). Melting points were obtained on a Fisher-Johns melting point apparatus and are uncorrected. Flash column chromatography on silica gel (60 Å, 230-400 mesh, obtained from Silicycle Inc.) was performed with reagent grade solvents. Analytical thin layer chromatography (TLC) was performed on pre-coated aluminum-backed silica gel plates (Alugram SIL G/UV254 purchased from Rose Scientific Limited or Silicycle Inc.) and visualized using KMnO_4 , or ninhydrin, or Hanessian's Stain and heating. All microwave irradiation experiments were conducted in Initiator™ microwave apparatus operating at a frequency of 2.45 GHz with continuous irradiation power from 0 to 300 W utilizing the standard absorbance level of 300 W maximum power.

Experimental Section:

General Epoxidation Reaction Condition: To a solution of diene (10.0 mmol) in CH₂Cl₂ (50 mL, 0.5 M) at 0 °C (ice bath) was added 77% pure *m*CPBA (2.46 g, 11.0 mmol, 1.1 eq) and the reaction was stirred for 2 h. Saturated solution of Na₂SO₃ (25 mL) was then added and the aqueous layer was extracted once with CH₂Cl₂. The organic layer was then washed with a 0.1 M solution of NaOH (25 mL), followed with saturated brine (25 mL). The organic layer was then dried with MgSO₄, filtered, and evaporated to give the epoxides, which were either purified by flash chromatography or used without further purification.

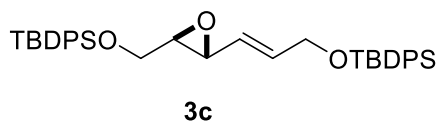
The following epoxides were prepared using the above general procedure:



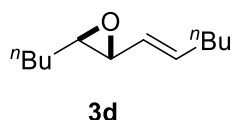
***tert*-Butyl(((*E*)-3-((2*R**,3*R**)-3-methyloxiran-2-yl)allyl)oxy)diphenylsilane (3a) and *tert*-Butyldiphenyl(((2*R**,3*R**)-3-((*E*)-prop-1-en-1-yl)oxiran-2-yl)methoxy)silane (3b):** The crude products were purified by flash chromatography on silica gel using 20:1 hexanes-ethyl acetate afforded **3a** (1.59 g, 41%) and **3b** (1.16 g, 30%).

3a: Colourless oil, $R_f = 0.25$ (20:1 Hexanes: EtOAc); ¹H NMR (300 MHz, CDCl₃) δ 7.65 – 7.68 (4H, m), 7.34 – 7.45 (6H, m), 5.97 (1H, ddd, $J = 15.5, 4.5, 4.5$ Hz), 5.53 (1H, dd, $J = 15.5, 8.0, 2.0$ Hz), 4.19 – 4.23 (2H, m), 3.08 (1H, dd, $J = 8.0, 2.0$ Hz), 2.90 (1H, qd, $J = 5.5, 2.0$ Hz), 1.34 (3H, d, $J = 5.5$ Hz), 1.06 (9H, s); ¹³C NMR (100 MHz, CDCl₃) δ 135.7, 133.8, 133.7, 129.9, 127.9, 127.9, 63.9, 56.9, 54.7, 27.0, 19.5, 13.6; IR (film) ν 2930, 2858, 1427, 1113, 702 cm⁻¹; MS (EI) m/e (relative intensity): 295.1 (25), 217.1 (19), 199.1 (100), 57.1 (17); HRMS (EI): m/z calcd for C₁₈H₁₉O₂Si (-C₄H₉): 295.1154, found 295.1160.

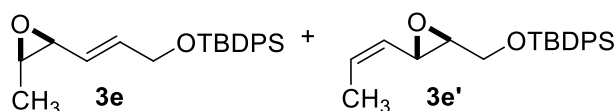
3b: Colourless oil, $R_f = 0.35$ (20:1 Hexanes: EtOAc); ¹H NMR (300 MHz, CDCl₃) δ 7.66 – 7.70 (4H, m), 7.36 – 7.43 (6H, m), 5.90 (1H, dq, $J = 15.5, 6.5$ Hz), 5.20 (1H, ddq, $J = 15.5, 8.0, 1.5$ Hz), 3.81 (1H, dd, $J = 12.0, 3.5$ Hz), 3.77 (1H, dd, $J = 12.0, 4.5$ Hz), 3.19 (1H, dd, $J = 8.0, 2.0$ Hz), 3.03 (1H, ddd, $J = 4.5, 3.5, 2.0$ Hz), 1.79 (3H, dd, $J = 6.5, 1.5$ Hz), 1.06 (9H, s); ¹³C NMR (100 MHz, CDCl₃) δ 135.9, 135.8, 133.6, 133.5, 132.1, 130.0, 128.4, 128.0, 127.9, 64.1, 60.2, 56.4, 27.0, 19.5, 18.1; IR (film) ν 2932, 2858, 1427, 1112, 702 cm⁻¹; MS (EI) m/e (relative intensity): 295.1 (9), 251.1 (10), 217.1 (10), 200.1 (17), 199.1 (100), 197.1 (9), 86.0 (10), 84.0 (16); HRMS (EI): m/z calcd for C₁₈H₁₉O₂Si (-C₄H₉): 295.1154, found 295.1147.



tert-Butyl(((E)-3-((2R*,3R*)-3-(((tert-butyldiphenylsilyl)oxy)methyl)oxiran-2-yl)allyl)oxy)-diphenylsilane (3c): The crude epoxide **3c** was immediately used without further purification.



(2R*,3R*)-2-Butyl-3-((E)-hex-1-en-1-yl)oxirane (3d): Vinyl epoxide **3d** was synthesized from literature procedure¹ and was used without further purification.

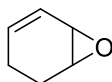


tert-Butyl(((E)-3-((2S*,3R*)-3-methyloxiran-2-yl)allyl)oxy)diphenylsilane (3e) and tert-Butyldiphenyl(((2S*,3S*)-3-((Z)-prop-1-en-1-yl)oxiran-2-yl)methoxy)silane (3e'): The crude products were purified by flash chromatography on silica gel using 20:1 hexanes-ethyl acetate afforded **3e** (0.995 g, 45%) and **3e'** (0.498 g, 23%).

3e: $R_f = 0.25$ (20:1 Hexanes: EtOAc); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.65 – 7.69 (4H, m), 7.35–7.44 (6H, m), 6.00 (1H, ddd, $J = 15.5, 4.5, 4.5$ Hz), 5.71 (1H, ddt, $J = 15.5, 7.5, 2.0$ Hz), 4.24 – 4.27 (2H, m), 3.43 (1H, dd, $J = 7.5, 4.5$ Hz), 3.21 (1H, ddd, $J = 11.0, 5.5, 4.5$ Hz), 1.23 (3H, d, $J = 5.5$ Hz), 1.05 (9H, s); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 135.7, 133.8, 133.7, 129.9, 127.9, 127.9, 63.9, 56.9, 54.7, 27.0, 19.5, 13.6; IR (film) ν 2931, 2857, 1427, 1113, 702 cm^{-1} ; MS (EI) m/e (relative intensity): 295.1 (52), 251.1 (13), 217.1 (47), 199.1 (100), 197.1 (14), 57.1 (30); HRMS (EI): m/z calcd for $\text{C}_{18}\text{H}_{19}\text{O}_2\text{Si}$ ($-\text{C}_4\text{H}_9$): 295.1154, found 295.1150.

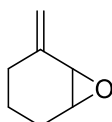
3e': $R_f = 0.35$ (20:1 Hexanes: EtOAc); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.65 – 7.70 (4H, m), 7.36 – 7.46 (6H, m), 5.79 (1H, ddq, $J = 11.0, 7.0, 1.0$ Hz), 5.07 – 5.13 (1H, m), 3.87 (1H, dd, $J = 12.0, 3.5$ Hz), 3.79 (1H, dd, $J = 12.0, 4.5$ Hz), 3.58 (1H, dd, $J = 9.0, 1.5$ Hz), 3.06 (1H, ddd, $J = 5.5, 4.5, 1.5$ Hz), 1.78 (3H, dd, $J = 7.0, 2.0$ Hz), 1.05 (9H, s); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 135.8, 135.8, 133.5, 131.4, 130.0, 128.0, 127.9, 127.5, 64.0, 60.1, 51.8, 27.0, 19.5, 13.6; IR (film) ν 2930, 2857, 1427, 1113, 702 cm^{-1} ; MS (EI) m/e (relative intensity): 228.1 (24), 227.1

(100), 213.1 (71), 199.1 (27), 183.1 (78), 181.1 (22), 57.1 (25); HRMS (EI): m/z calcd for $C_{18}H_{19}O_2Si$ (- C_4H_9): 295.1154, found 295.1155.



3f

7-Oxabicyclo [4.1.0] hept-2-ene (3f): To a solution of diene (1.2 g, 15.0 mmol) in CH_2Cl_2 (50 mL) at 0 °C (ice bath) was added 77% pure *m*CPBA (3.7 g, 16.5 mmol) and then the reaction mixture was stirred for 2 h. A saturated solution of Na_2SO_3 (25 mL) was then added and the aqueous layer was extracted once with CH_2Cl_2 . The organic layer was then washed with a saturated solution of K_2CO_3 (25 mL), followed with saturated brine (25 mL). The organic layer was then dried with $MgSO_4$, filtered, and evaporated to give the crude epoxide **3f** which was immediately used without further purification. 1H NMR (400 MHz, $CDCl_3$) δ 5.97 (1H, dt, J = 9.9, 3.3 Hz), 5.94 – 5.88 (1H, m), 3.51 – 3.52 (1H, m), 3.24 (1H, td, J = 4.1, 1.8 Hz), 2.22 – 2.28 (1H, m), 1.98 – 2.13 (2H, m), 1.58 – 1.65 (1H, m). The spectral data were in full accordance with those reported in the literature.²



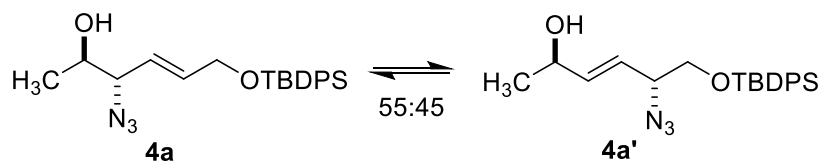
3g

2-Methylene-7-oxabicyclo[4.1.0]heptane (3g): Vinyl epoxide **3g** was synthesized from literature procedure³ and was used without further purification.

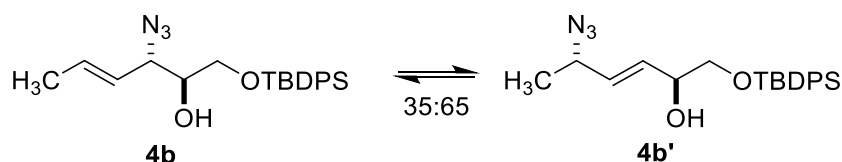
General Epoxide Ring Opening Reaction (Method A):

Adapted from the procedure of Wipf and coworkers.⁴ To a solution of epoxide (2 mmol) in ethanol (10 mL, 0.2 M) was added NaN_3 (0.390 g, 6.0 mmol, 3.0 eq.) and NH_4Cl (0.321 g, 6.0 mmol, 3.0 eq.). The reaction was slowly heated to reflux (over about 1.5 h) and stirred at reflux for another 1 h. The solution was then cooled to room temperature, filtered and washed with ethanol (2 x 5 mL), and the solvent was evaporated. Et_2O (15 mL) was added and the organic layer was extracted with water. The aqueous layer was then washed with Et_2O (2 x 10 mL) and the combined organic layers were dried, filtered, and solvent evaporated. Flash

chromatography on silica gel (2:1, Hexanes: EtOAc) gave the allylic azides as mixtures of regioisomers.

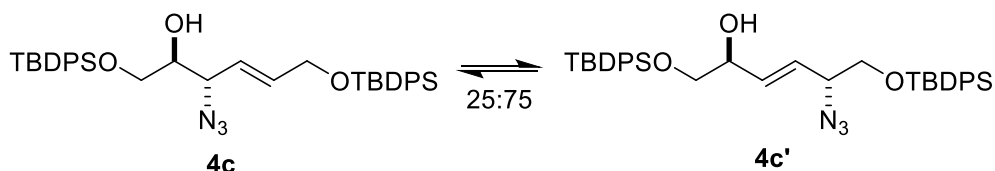


(2R*,3S*,E)-3-Azido-6-((tert-butyldiphenylsilyloxy)hex-4-en-2-ol (4a) and (2R*,5R*,E)-5-Azido-6-((tert-butyldiphenylsilyloxy)hex-3-en-2-ol (4a'): To vinyl epoxide **3a** (0.464 g, 1.32 mmol) dissolved in EtOH (15 mL) was added sodium azide (0.257 g, 3.95 mmol, 3.0 eq.) and ammonium chloride (0.211 g, 3.95 mmol, 3.0 eq.). The reaction mixture was slowly brought to reflux and refluxed at room temperature for 1 h following work up as in the general epoxide ring opening reaction. Purification by flash column chromatography on silica gel afforded **4a** and **4a'** in a 55:45 ratio as a colourless oil (0.450 g, 87%), $R_f = 0.25$ and 0.30 (5:1 Hexanes: EtOAc). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.66 – 7.69 (4H, m, **a** and **a'**), 7.36 – 7.46 (6H, m, **a** and **a'**), 5.92 (0.55H, ddd, $J = 15.5, 4.0, 4.0$ Hz, **a**), 5.77 – 5.85 (1H, m, **a** and **a'**), 5.55 (0.45H, ddd, $J = 15.5, 7.0, 1.0$ Hz, **a'**), 4.26 – 4.34 (0.45H, m, **a'**), 4.27 – 4.29 (1.1H, m, **a**), 3.96 – 4.02 (0.45H, m, **a'**), 3.91 (0.55H, dd, $J = 8.0, 4.5$ Hz, **a**), 3.74 – 3.82 (0.55H, m, **a**), 3.71 (0.45H, dd, $J = 10.5, 4.5$ Hz, **a'**), 3.66 (0.45H, dd, $J = 10.5, 7.0$ Hz, **a'**), 1.77 (0.45H, d, $J = 5.0$ Hz, **a'**), 1.40 (0.55H, d, $J = 4.5$ Hz, **a**), 1.26 (1.65H, d, $J = 6.5$ Hz, **a**), 1.16 (1.35 H, d, $J = 6.0$ Hz, **a'**), 1.07 (9H, s, **a** and **a'**); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 139.2, 136.7, 135.9, 135.8, 135.7, 133.7, 133.6, 133.2, 130.1, 130.1, 130.0, 128.0, 128.0, 128.0, 124.3, 123.1, 69.8, 69.4, 68.2, 66.9, 64.8, 63.6, 27.0, 27.0, 23.6, 19.5, 19.4, 18.7; IR (film) ν 3392, 2932, 2856, 2101, 1472, 1426, 1259, 1113, 701 cm^{-1} ; MS (EI) m/e (relative intensity): 323.2 (4), 292.1 (5), 266.1 (4), 219.0 (7), 200.1 (15), 199.1 (100), 181.0 (7), 135.1 (3); HRMS (EI): m/z calcd for $\text{C}_{18}\text{H}_{20}\text{N}_3\text{O}_2\text{Si}$ ($-\text{C}_4\text{H}_9$): 338.1324, found 338.1325.

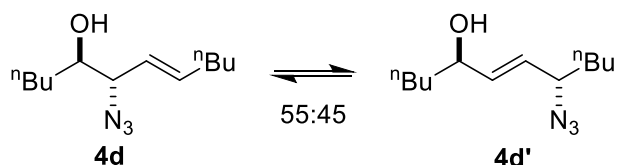


(2S*,3S*,E)-3-Azido-1-((tert-butyldiphenylsilyloxy)hex-4-en-2-ol (4b) and (2S*,5S*,E)-5-Azido-1-((tert-butyldiphenylsilyloxy)hex-3-en-2-ol (4b'): To vinyl epoxide **3b** (0.893 g, 2.53 mmol) dissolved in EtOH (20 mL) was added sodium azide (0.406 g, 7.5 mmol, 3.0 eq.) and ammonium chloride (0.500 g, 7.51 mmol, 3.0 eq.). The reaction was slowly brought to reflux

and refluxed at room temperature for 2 h following the work up for the general epoxide ring opening reaction. Purification by flash column chromatography on silica gel (2:1, hexanes: EtOAc) afforded **4b** and **4b'** in a 35:65 ratio as a pale yellow oil (0.761 g, 76%), $R_f = 0.40$ and 0.45 (5:1 Hex/EtOAc). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.63 – 7.67 (4H, m, **b** and **b'**), 7.37 – 7.46 (6H, m, **b** and **b'**), 5.81 (0.35H, ddq, $J = 15.0, 6.5, 0.5$ Hz, **b**), 5.73 (0.65H, ddd, $J = 15.5, 6.5, 1.0$ Hz, **b'**), 5.65 (0.65H, dd, $J = 15.5, 5.0$ Hz, **b'**), 5.50 (0.35H, ddq, $J = 15.0, 8.5, 1.5$ Hz, **b**), 4.25 – 4.30 (0.65H, m, **b'**), 3.98 – 4.01 (0.35H, m, **b**), 3.97 (0.65H, dq, $J = 6.5, 6.5$ Hz, **b'**), 3.71 (0.65H, dd, $J = 10.0, 3.5$ Hz, **b'**), 3.65 – 3.70 (1.05H, m, **b**), 3.55 (0.65H, dd, $J = 10.0, 7.0$ Hz, **b'**), 2.63 (0.65H, d, $J = 4.0$ Hz, **b'**), 2.42 (0.35H, d, $J = 4.5$ Hz, **b**), 1.77 (0.35H, dd, $J = 6.5, 1.5$ Hz, **b**), 1.27 (0.65H, d, $J = 6.5$ Hz, **b'**), 1.07 (9H, s, **b** and **b'**); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 135.8, 135.7, 133.2, 133.1, 131.4, 131.3, 130.2, 130.1, 128.1, 128.1, 125.0, 73.3, 72.1, 67.9, 65.8, 64.5, 59.0, 27.1, 20.1, 19.5, 19.5, 18.1 (missing 1 C); IR (film) ν 3443 (broad), 2926, 2856, 2101, 1426, 1242, 1110, 701 cm^{-1} ; MS (EI) m/e relative intensity: 295.1 (12), 290.1 (15), 241.1 (36), 223.1 (20), 200.1 (38), 199.1 (100), 181.0 (33), 163.0 (62), 135.1 (22); HRMS (EI): m/z calcd for $\text{C}_{22}\text{H}_{29}\text{N}_3\text{O}_2\text{NaSi}$: 418.1921, found 418.1923.

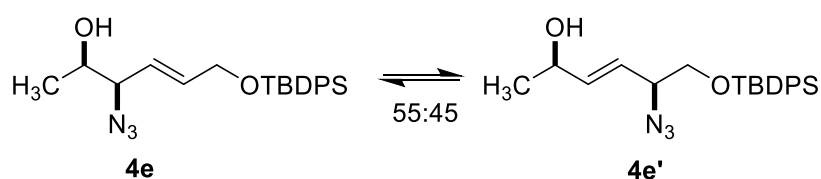


(*6S**,*7S**,*E*)-7-Azido-2,2,13,13-tetramethyl-3,3,12,12-tetraphenyl-4,11-dioxa-3,12-disilatetradec-8-en-6-ol (**4c**) and (*6S**,*9R**,*E*)-9-Azido-2,2,13,13-tetramethyl-3,3,12,12-tetraphenyl-4,11-dioxa-3,12-disilatetradec-7-en-6-ol (**4c'**): The general epoxide opening reaction protocol was used. The crude **4c** / **4c'** was immediately used without further purification.

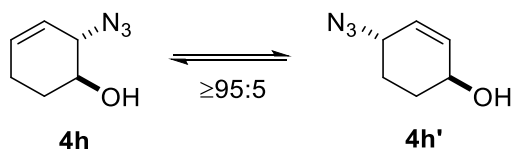


(*5R**,*6S**,*E*)-6-Azidododec-7-en-5-ol (**4d**) and (*5R**,*8S**,*E*)-8-Azidododec-6-en-5-ol (**4d'**): The general epoxide opening reaction protocol was used followed by chromatography performed on the crude material (4:1 Hexanes: EtOAc) to give **4d** and **4d'** in a 55:45 ratio as a pale yellow oil

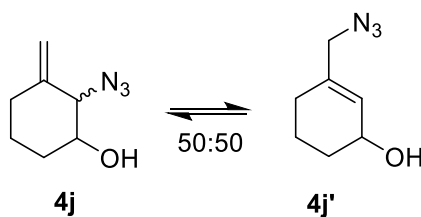
(59% yield, 2 steps). ^1H NMR (400 MHz, CDCl_3) δ 5.81 (0.55H, dt, $J = 15.5, 6.5$ Hz, **d**) 5.75 (0.45H, ddd, $J = 15.5, 6.0, 0.5$ Hz, **d'**) 5.79 (1H, ddd, $J = 15.5, 8.0, 1.0$ Hz, **d**), 5.62 (0.4H, ddt, $J = 15.5, 9.0, 1.5$ Hz, **d'**), 4.16 (0.45H, m, **d'**), 3.80 – 3.87 (1H, m, **d** and **d'**), 3.58 (0.55H, m, **d**), 2.10 – 2.16 (1.1H, m, **d**), 1.26 – 1.59 (10.9H, m, **d** and **d'**), 0.90 (6H, d, m, **d** and **d'**); ^{13}C NMR (75 MHz, CDCl_3) δ 139.2, 137.4, 128.4, 122.9, 73.0, 72.3, 69.6, 64.3, 37.2, 34.5, 32.7, 32.3, 31.5, 28.2, 28.0, 27.7, 22.8, 22.6, 22.3, 14.2, 14.1, 14.0; IR (film) ν 3418, 2957, 2932, 2096, 1464, 1244, 971 cm^{-1} .



(2*R,3*R**,*E*)-3-Azido-6-((*tert*-butyldiphenylsilyl)oxy)hex-4-en-2-ol (4e) and (2*R**,5*S**,*E*)-5-Azido-6-((*tert*-butyldiphenylsilyl)oxy)hex-3-en-2-ol (4e')**: To vinyl epoxide **3e** (0.556 g, 1.58 mmol) dissolved in EtOH (10 mL) was added sodium azide (0.305 g, 4.7 mmol, 3.0 eq.) and ammonium chloride (0.250 g, 4.7 mmol, 3.0 eq.). The reaction mixture was slowly brought to reflux and refluxed at room temperature for 2 h following the work up as for the general epoxide ring opening reaction. Purification by flash column chromatography on silica gel (2:1, hexanes: EtOAc) afforded **4e** and **4e'** in a 55:45 ratio as a colourless oil (0.54 g, 88%), $R_f = 0.25$ and 0.30 (5:1 Hexanes: EtOAc). ^1H NMR (300 MHz, CDCl_3) δ 7.66 – 7.69 (4H, m, **e** and **e'**), 7.35 – 7.47 (6H, m, **e** and **e'**), 5.92 (0.55H, ddd, $J = 15.5, 4.0, 4.0$ Hz, **e**), 5.83 (0.45H, ddd, $J = 15.5, 6.0, 1.0$ Hz, **e'**), 5.75 (0.55H, ddt, $J = 15.5, 8.5, 2.0$ Hz, **e**), 5.55 (0.45H, ddd, $J = 15.5, 7.0, 1.0$ Hz, **e'**), 4.26 – 4.34 (0.45H, m, **e'**), 4.26 – 4.28 (1.1H, m, **e**), 3.96 – 4.02 (0.45H, m, **e'**), 3.78 (0.55H, dd, $J = 8.0, 8.0$ Hz, **e**), 3.71 (0.45H, dd, $J = 10.5, 4.5$ Hz, **e'**), 3.65 (0.45H, dd, $J = 10.5, 7.0$ Hz, **e'**), 3.62 – 3.68 (0.45H, m, **e'**), 1.26 (1.65H, d, $J = 6.5$ Hz, **e'**), 1.16 (1.35H, d, $J = 6.0$ Hz, **e**), 1.07 (9H, s, **e** and **e'**); ^{13}C NMR (75 MHz, CDCl_3) δ 139.2, 136.1, 135.9, 135.8, 133.3, 130.1, 130.0, 128.0, 128.0, 128.0, 124.3, 123.8, 76.8, 71.1, 69.8, 68.2, 66.9, 64.7, 63.5, 27.0, 27.0, 23.5, 19.5, 19.4; IR (film) ν 3395 (br), 2930, 2857, 2101, 1471, 1426, 1242, 1110, 699 cm^{-1} ; MS (EI) m/e (relative intensity): 292.1 (4), 200.1 (16), 199.1 (100), 181.0 (8), 163 (4); HRMS (EI): m/z calcd for $\text{C}_{22}\text{H}_{29}\text{N}_3\text{O}_2\text{NaSi}$: 418.1921, found 418.1913.



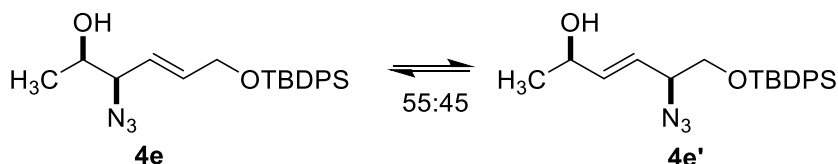
(1*S,2*S**)-2-Azidocyclohex-3-en-1-ol (4h):** The general epoxide opening protocol was used followed by work up and chromatography performed on the crude material (2:1 Hexanes: EtOAc) to give **4h** and **4h'** in $\geq 95:5$ ratio as a colourless oil (58% yield). $R_f = 0.40$ (2:1 Hex/EtOAc). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 5.88 – 5.93 (1H, m), 5.55– 5.60 (1H, m), 3.83 (1H, dt, $J = 7.2, 2.4$ Hz), 3.74 (1H, ddd, $J = 10.8, 7.4, 3.5$ Hz), 2.16 – 2.22 (3H, m), 1.93 – 2.00 (1H, m), 1.66 – 1.72 (1H, m); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 131.6, 123.2, 71.1, 64.4, 28.7, 24.2; IR (film) ν 3359, 2930, 2098 cm^{-1} ; HRMS (DART): m/z calcd for $\text{C}_6\text{H}_{13}\text{N}_4\text{O}$ [$\text{M} + \text{NH}_4$] $^+$: 157.1089, found 157.1089.



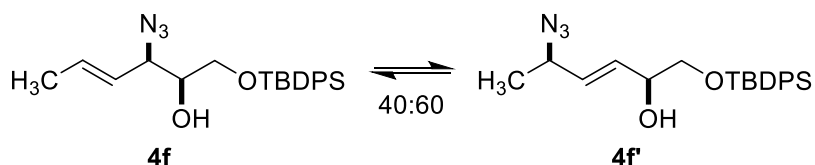
2-Azido-3-methylenecyclohexanol (4j) and 3-(azidomethyl)cyclohex-2-enol (4j'): The crude vinyl epoxide **3g** (0.356 g, 3.23 mmol) was dissolved in 25 mL of EtOH and sodium azide (0.63 g, 9.7 mmol, 3 eq.) and ammonium chloride (0.519 g, 9.7 mmol, 3 eq.) was added. The reaction was slowly brought to reflux and refluxed at room temperature for 2 h following the work up as in the general epoxide ring opening reaction. Purification by flash column chromatography on silica gel afforded **4j** and **4j'** in a 50:50 ratio as a pale yellow oil (0.336 g, 67%), $R_f = 0.40$ and 0.45 (5:1 Hex/EtOAc). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 5.77 – 5.81 (0.5H, m, **j'**), 4.95 – 5.05 (1H, m, **j**), 4.24 – 4.32 (0.5H, m, **j'**), 4.21 (0.2H, d, $J = 3.5$ Hz, **j**), 3.70 – 3.80 (0.5H, m, **j**), 3.65 – 3.75 (1H, m, **j'**), 3.39 – 3.50 (0.3H, m, **j**), 1.20 – 2.05 (6H, m, **j'** and **j**); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 143.7, 136.4, 136.4, 128.7, 113.9, 110.3, 74.0, 71.6, 71.2, 70.0, 65.8, 57.0, 33.7, 32.5, 31.8, 30.4, 30.2, 26.8, 23.8, 23.5, 19.1; IR (film) ν 3355, 2941, 2865, 2103, 1268, 1064 cm^{-1} ; MS (DART) m/e (relative intensity): 171.1 (65), 153.1 (50), 126.1 (50), 108.1 (100); HRMS (DART): m/z calcd for $\text{C}_7\text{H}_{15}\text{N}_4\text{O}$ ($\text{M} + \text{NH}_4$) $^+$: 171.1245, found 171.1250.

General Condition for Palladium-Catalyzed Opening of Vinyl Epoxides (Method B):

Adapted from the procedure of Miyashita and coworkers.⁵ To a stirred solution of vinyl epoxide (1.0 mmol) in THF (10 mL, 0.1 M) under N₂ gas inlet at room temperature was added TMSN₃ (0.28 mL, 2.0 mmol, 2.0 eq.). The mixture was stirred for 5 min and Pd(PPh₃)₄ (116 mg, 0.10 mmol, 10 mol%) was added. The reaction was stirred overnight (14 h), and then a solution of 10% citric acid in MeOH (10 mL) was added. The solution was stirred for 1 h at ambient temperature, and then concentrated in vacuo. The residue was dissolved in ether, and passed through a celite column using ether as a solvent, followed by evaporation of the solvent in vacuo. The residue was purified by silica gel column chromatography (hexane/EtOAc = 2:1) to afford the hydroxyl allylic azides.

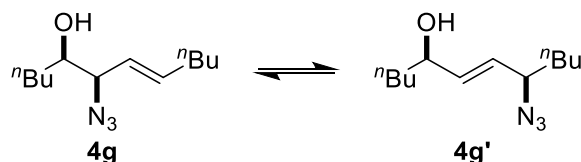


(2R*,3R*,E)-3-Azido-6-(tert-butyldiphenylsilyloxy)hex-4-en-2-ol (4e) and (2R*,5S*,E)-5-Azido-6-(tert-butyldiphenylsilyloxy)hex-3-en-2-ol (4e'): To vinyl epoxide 3a (0.352 g, 1.0 mmol) dissolved in THF (10 mL) was added TMSN₃ (0.28 mL, 2.0 mmol, 2.0 eq.) and Pd(PPh₃)₄ (116 mg, 0.10 mmol, 10 mol%). The reaction mixture was stirred at room temperature for 14 h and then a solution of 10% citric acid in MeOH (10 mL) was added. The solution was stirred for 1 h at ambient temperature, and then concentrated in vacuo. The residue was dissolved in ether and passed through a celite column using ether as a solvent, followed by evaporation of the solvent in vacuo. Purification by flash column chromatography by silica gel (2:1, hexanes: EtOAc) afforded 4e / 4e' in a 55:45 ratio as a colourless oil (0.284 g, 72%). Characterization data were identical with the above reported data for 4e / 4e' using method A.

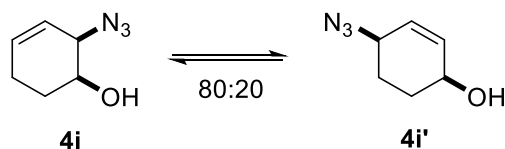


(2S*,3R*,E)-3-Azido-1-(tert-butyldiphenylsilyloxy)hex-4-en-2-ol (4f') and (2S*,5R*,E)-5-Azido-1-(tert-butyldiphenylsilyloxy)hex-3-en-2-ol (4f): To vinyl epoxide 3b (0.368 g, 1.04 mmol) dissolved in THF (10 mL) was added TMSN₃ (0.265 mL, 2.08 mmol, 2.0 eq.) and

Pd(PPh₃)₄ (115 mg, 0.10 mmol, 10 mol%). The reaction mixture was stirred at room temperature for 14 h and then a solution of 10% citric acid in MeOH (10 mL) was added. The solution was stirred for 1 h at ambient temperature, and then concentrated in vacuo. The residue was dissolved in ether and passed through a celite column using ether as a solvent, followed by evaporation of the solvent in vacuo. Purification by flash column chromatography by silica gel (2:1, hexanes: EtOAc) afforded **4f/ 4f'** in a 40:60 ratio as a pale yellow oil (0.273 g, 66%), *R_f* = 0.40 and 0.45 (5:1 Hex/EtOAc). ¹H NMR (300 MHz, CDCl₃) δ 7.61 – 7.67 (4H, m, **f** and **f'**), 7.36 – 7.47 (6H, m, **f** and **f'**), 5.92 (0.6H, dq, *J* = 15.5, 4.0 Hz, **f**), 5.83 (0.4H, ddd, *J* = 15.5, 5.5, 1.0 Hz, **f'**), 5.75 (0.6H, ddt, *J* = 15.5, 8.5, 2.0 Hz, **f'**), 5.55 (0.4H, ddd, *J* = 15.5, 7.0, 1.0 Hz, **f**), 4.23 – 4.30 (0.6H, m, **f'**), 4.27 (0.6H, dd, *J* = 4.0, 2.0 Hz, **f**); 3.93 – 4.04 (1H, m, **f** and **f'**), 3.52 – 3.73 (2.4H, m, **f** and **f'**), 2.62 (0.6H, d, *J* = 4.0 Hz, **f'**), 2.42 (0.4H, d, *J* = 5.5 Hz, **f**), 1.73 (1.2H, dd, *J* = 6.5, 1.5 Hz, **f**), 1.26 (1.8H, d, *J* = 6.5 Hz, **f'**), 1.07 (9H, s, **f** and **f'**); ¹³C NMR (75 MHz, CDCl₃) δ 135.8, 135.8, 133.2, 133.1, 132.6, 131.3, 131.2, 130.1, 128.1, 128.0, 125.4, 73.8, 72.1, 67.9, 66.4, 64.6, 58.8, 27.1, 20.1, 19.5, 18.0 (missing 1 C); IR (film) ν 3445 (br), 2930, 2857, 2101, 1242, 1110, 699 cm⁻¹; MS (EI) *m/e* (relative intensity): 295.1 (37), 241.1 (14), 200.1 (19), 199.1 (100), 181.0 (17), 163.0 (24), 135.1 (6); HRMS (EI): *m/z* calcd for C₁₈H₂₀N₃O₂SiO (-C₄H₉): 338.1329, found 338.1325.



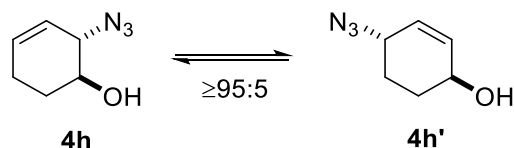
(5*R,6*R**,*E*)-6-azidododec-7-en-5-ol (4g) and (5*R**,8*R**,*E*)-8-azidododec-6-en-5-ol (4g')**: To vinyl epoxide **3d** (0.149 g, 0.82 mmol) dissolved in THF (10 mL) was added TMSN₃ (0.22 g, 3.95 mmol, 2.0 eq.) and Pd(PPh₃)₄ (95 mg, 0.082 mmol, 10 mol%). The reaction mixture was stirred at room temperature for 14 h and then a solution of 10% citric acid in MeOH (10 mL) was added. The solution was stirred for 1 h at ambient temperature, and then concentrated in vacuo. The residue was dissolved in ether and passed through a celite column using ether as a solvent, followed by evaporation of the solvent in vacuo. Purification by flash column chromatography on silica gel (2:1, hexanes: EtOAc) failed to give pure compounds, and the crude compound was carried directly to the next step.



(1*S,2*R**)-2-Azidocyclohex-3-enol (4i) and (1*S**,4*R**)-4-Azidocyclohex-3-enol (4i'):**

To a solution of vinyl epoxide **3f** (300 mg, 3.12 mmol) in THF (20 mL), was added TMSN₃ (0.85 g, 6.25 mmol), followed by addition of Pd(PPh₃)₄ (360 mg, 0.312 mmol). The reaction mixture was stirred at room temperature for 14 h and then a solution of 10% citric acid in MeOH (15 mL) was added. The solution was stirred for 1 h at ambient temperature, and then concentrated in vacuo. The residue was dissolved in ether (40 mL) and washed with water (15 mL). The organic layer was then dried with MgSO₄, filtered, and evaporated. Purification by flash chromatography (2:1, Hexanes: EtOAc) gave the allylic azides as a mixture of regioisomers **4i** / **4i'** (80:20) as a pale-yellow oil (270 mg, 62%), *R_f* = 0.40 (2:1 Hex/EtOAc). IR (film) ν 3380, 2934, 2098, 1254 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 6.00 – 6.07 (1H, m), 5.78 – 5.83 (0.20H, m), 5.69 – 5.76 (0.80H, m), 4.15 – 4.21 (0.20H, m), 4.00 – 4.01 (0.80H, m), 3.84 – 3.93 (1H, m), 2.22 – 2.34 (1H, m), 2.06 – 2.19 (1H, m), 1.67 – 1.91 (3H, m); ¹³C NMR (100 MHz, CDCl₃) δ 134.7, 133.7, 127.5, 121.9, 68.9, 65.0, 60.0, 55.7, 28.6, 26.7, 25.3, 24.2; HRMS (DART): *m/z* calcd for C₆H₁₃N₄O [M + NH₄]⁺: 157.1089, found 157.1085.

Epoxide Ring Opening Reaction (Method C):

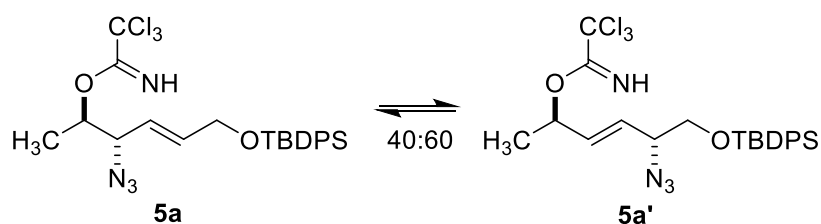


(1*S,2*S**)-2-Azidocyclohex-3-en-1-ol (4h):** To a stirred solution of crude epoxide **3f** (0.60 g, 6.25 mmol) in MeOH (20 mL) was added sodium azide (1.22 g, 18.7 mmol) and zinc chloride (2.54 g, 18.7 mmol). The reaction mixture was stirred at room temperature overnight, filtered through a pad of celite and the filtrate concentrated under reduced pressure. Then Et₂O (30 mL) was added and the organic layer was extracted with water (15 mL). The aqueous layer was washed with Et₂O (2 x 20 mL) and the combined organic layers were dried, filtered, and the solvent evaporated. Flash chromatography on silica gel (2:1, Hexanes: EtOAc) gave the allylic azides **4h** / **4h'** (0.59 g, 68%) as a mixture of regioisomers ($\geq 95:5$) as colourless oil. *R_f* = 0.40 (2:1 Hex/EtOAc). ¹H NMR (400 MHz, CDCl₃) δ 5.88 – 5.93 (1H, m), 5.55– 5.60 (1H, m), 3.83 (1H, dt, *J* = 7.2, 2.4 Hz), 3.74 (1H, ddd, *J* = 10.8, 7.4, 3.5 Hz), 2.16 – 2.22 (3H, m), 1.93

– 2.00 (1H, m), 1.66 – 1.72 (1H, m); ^{13}C NMR (100 MHz, CDCl_3) δ 131.6, 123.2, 71.1, 64.4, 28.7, 24.2; IR (film) ν 3359, 2930, 2098 cm^{-1} ; HRMS (DART): m/z calcd for $\text{C}_6\text{H}_{13}\text{N}_4\text{O}$ [$\text{M} + \text{NH}_4$] $^+$: 157.1089, found 157.1089.

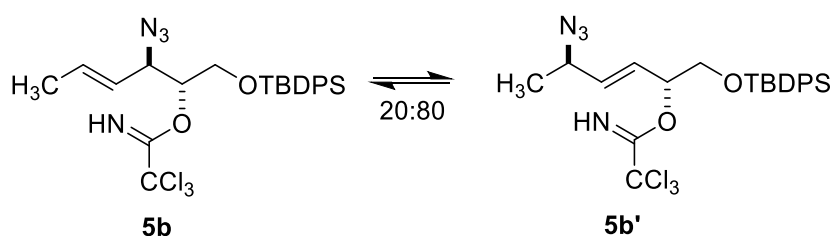
General Conditions for Formation of Allylic Trichloroacetimidates:

Adapted from the procedure of Overman.⁶ To a stirred solution of hydroxy allylic azide (1.0 mmol) at 0 °C in CH_2Cl_2 (10 mL, 0.1 M) was added DBU (0.23 mL, 1.5 mmol, 1.5 eq.), followed by dropwise addition of trichloroacetonitrile (0.18 mL, 1.8 mmol, 1.8 eq.). The solution was warmed to room temperature over 1.5–2 h, during which the solution turned orange-brown in colour. A solution of saturated ammonium chloride (15 mL) was added to the solution and the solution was extracted with dichloromethane (3 x 10 mL). The combined organic layers were dried with MgSO_4 and the solution filtered through a short column of silica gel. The solvent was then evaporated in vacuo, and the crude product was purified by silica gel column chromatography to afford allylic trichloroacetimidates.



(4*R,5*S**,*E*)-4-Azido-1-(*tert*-butyldiphenylsilyloxy)-5-(2,2,2-trichloroacetoxy)hex-4-ene (5a) and (2*R**,5*R**,*E*)-2-Azido-1-(*tert*-butyldiphenylsilyloxy)-5-(2,2,2-trichloroacetoxy) hex-3-ene (5a')**: To a stirred solution of hydroxy allylic azides **4a** / **4a'** (0.398 g, 1.01 mmol) at 0 °C in CH_2Cl_2 (10 mL) was added DBU (0.22 mL, 1.5 mmol, 1.5 eq.), followed by dropwise addition of trichloroacetonitrile (0.18 mL, 1.8 mmol, 1.8 eq.). The solution was warmed to room temperature and stirred for 1 h, during which the solution turned orange in colour. A solution of saturated ammonium chloride (6 mL) was added to the solution and the solution was extracted with dichloromethane (3 x 10 mL). The combined organic layers were dried with MgSO_4 and the solution filtered through a short column of silica gel. The solvent was then evaporated in vacuo, and the crude product was purified by silica gel column chromatography (5:1, Hexanes: EtOAc) to afford pure allylic azides **5a** / **5a'** in a 40:60 ratio as a pale yellow oil (0.455 g, 84%), R_f = 0.50 and 0.55 (10:1 Hex/EtOAc). ^1H NMR (400 MHz, CDCl_3) δ 8.38 (0.4H s, **a**), 8.31 (0.6H, s, **a'**), 7.66 – 7.69 (4H, m, **a** and **a'**), 7.36 – 7.44 (6H,

m, **a** and **a'**), 5.91 – 5.99 (0.8H, m, **a**), 5.87 (0.6H, dd, $J = 15.5, 5.5$, Hz, **a'**), 5.75 (0.6H, dd, $J = 15.5, 6.5$ Hz, **a'**), 5.50 (0.6H, dq, $J = 6.5, 6.5$ Hz, **a'**), 5.13 (0.4H, dq, $J = 6.0, 4.0$ Hz, **a**), 4.25 – 4.28 (0.8H, m, **a**), 4.18 (0.4H, dd, $J = 5.5, 4.0$ Hz, **a**), 4.00 (0.6H, ddd, $J = 6.5, 6.5, 4.5$ Hz, **a'**), 3.71 (0.6H, dd, $J = 10.5, 4.5$ Hz, **a'**), 3.66 (0.6H, dd, $J = 10.5, 6.5$ Hz, **a'**), 1.43 (1.8H, d, $J = 6.5$ Hz, **a'**), 1.32 (1.2H, d, $J = 6.0$ Hz, **a**), 1.07 (9H, s, **a** and **a'**); ^{13}C NMR (100 MHz, CDCl_3) δ 162.1, 161.8, 135.9, 135.9, 135.7, 133.7, 133.2, 133.2, 130.1, 130.1, 128.0, 128.0, 126.6, 122.4, 76.8, 74.8, 66.8, 66.4, 64.6, 63.4, 27.1, 27.0, 20.0, 19.5, 19.4, 14.9 (missing 2 C); IR (film) ν 3392, 2932, 2856, 2101, 1472, 1426, 1259, 1113, 701 cm^{-1} ; MS (ESI) m/e (relative intensity): 561.1 (10), 432.2 (22), 418.2 (34), 382.2 (23), 350.2 (100), 323.2 (45), 267.1 (18); HRMS (EI): m/z calcd for $\text{C}_{24}\text{H}_{29}\text{N}_4\text{O}_2\text{NaSiCl}_3$ ($\text{M}^{(35}\text{Cl}_3)+\text{Na}^+$): 561.1017, found 561.1011.

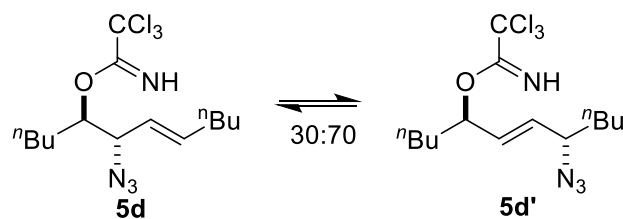


(2*R,3*R**,*E*)-3-Azido-1-(*tert*-butyldiphenylsilyloxy)-2-(2,2,2-trichloroacetoxy)hex-4-ene (**5b**) and (2*R**,5*R**,*E*)-5-azido-1-(*tert*-butyldiphenylsilyloxy)-2-(2,2,2-trichloroacetoxy) hex-3-ene (**5b'**):** To a stirred solution of hydroxy allylic azides **4b** / **4b'** (0.248 g, 0.63 mmol) at 0 °C in CH_2Cl_2 (6 mL) was added DBU (0.14 mL, 0.94 mmol, 1.5 eq.), followed by dropwise addition of trichloroacetonitrile (0.11 mL, 1.13 mmol, 1.8 eq.). The solution was warmed to room temperature and stirred for 2 h, during which the solution turned orange-brown in colour. A solution of saturated ammonium chloride (6 mL) was added to the solution and the solution was extracted three times with dichloromethane. The combined organic layers were dried with MgSO_4 and then the solution was filtered through a short column of silica gel. The solvent was then evaporated in vacuo, and the crude mixture was purified by silica gel column chromatography to afford allylic azides **5b** / **5b'** in a 20:80 ratio (5% of another isomer which was identified as *cis* isomer is also observed) as a pale yellow oil (0.320 g, 95%), $R_f = 0.50$ and 0.55 (15:1, Hexanes: EtOAc). ^1H NMR (400 MHz, CDCl_3) (only peaks for major isomer was listed) δ 8.37 (1H, s), 7.64 – 7.73 (4H, m), 7.34 – 7.46 (6H, m), 5.84 (1H, dd, $J = 15.5, 6.0$ Hz), 5.78 (1H, dt, $J = 15.5, 5.0$ Hz), 5.30 – 5.78 (1H, m), 3.96 – 4.04 (2H, m), 3.78 – 3.94 (2H, m), 1.29 (3H, d, $J = 6.5$ Hz), 1.07 (9H, s); ^{13}C NMR (75 MHz, CDCl_3) δ 162.0, 136.2, 135.9, 135.9, 133.4, 133.2, 130.0, 130.0, 128.0, 128.0, 127.2, 78.8, 65.3, 58.8, 27.0, 20.1, 19.5

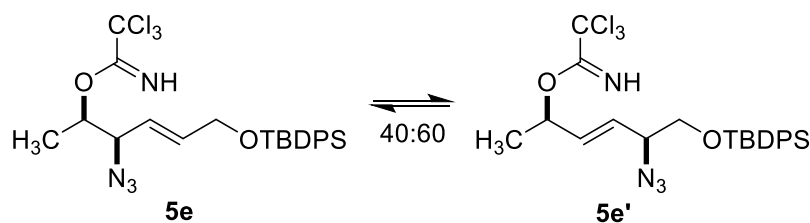
(missing 1 C); IR (film) ν 3344, 2959, 2931, 2858, 2104, 1664, 1295, 1114, 796, 701 cm^{-1} ; MS (DART) m/e (relative intensity): 556.1 (90, $(\text{M}^{(35}\text{Cl}_3)+\text{H})^+$), 378.2 (39), 350.2 (100), 335.2 (61); HRMS (EI): m/z calcd for $\text{C}_{24}\text{H}_{33}\text{Cl}_3\text{N}_5\text{O}_2\text{Si}$ ($\text{M}^{(35}\text{Cl}_3)+\text{H})^+$: 539.1203, found 539.1204.



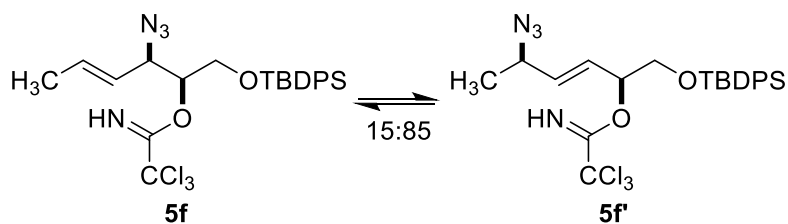
(4*R,5*S**,*E*)-4-Azido-1,6-di(*tert*-butyldiphenylsilyloxy)-5-(2,2,2-trichloroacetoxy)hex-4-ene (5c) and (2*R**,5*R**,*E*)-2-Azido-1,6-di(*tert*-butyldiphenylsilyloxy)-5-(2,2,2-trichloroacetoxy)hex-3-ene (5c')**: To a stirred solution of hydroxy allylic azide **4c** / **4c'** (0.217 g, 0.34 mmol) at 0 °C in CH_2Cl_2 (5 mL) was added DBU (75 μL , 0.50 mmol, 1.5 eq.), followed by dropwise addition of trichloroacetonitrile (60 μL 0.60 mmol, 1.8 eq.). The solution was warmed to room temperature over 1.5 h, during which the solution turned orange in colour. A solution of saturated ammonium chloride (6 mL) was added to the solution and the solution was extracted with dichloromethane (3 x 5 mL). The combined organic layers were dried with MgSO_4 and the solution filtered through a short column of silica gel. The solvent was then evaporated in vacuo, and the crude mixture was purified by silica gel column chromatography (10:1, Hexanes: EtOAc) to afford compound **5c** / **5c'** as a 15:85 ratio (10% of another isomer which was identified as *cis* isomer is also observed) as a colourless oil (0.199 g, 75%), R_f = 0.80 and 0.85 (20:1 Hex: EtOAc). ^1H NMR (400 MHz, CDCl_3) (only peaks for major regioisomer are listed) δ 8.34 (1H, s), 7.63 – 7.69 (8H, m), 7.33 – 7.44 (12H, m), 5.74 – 5.86 (2H, m), 5.51 – 5.57 (1H, m), 3.96 – 4.01 (1H, m), 3.83 (1H, dd, J = 11.0, 6.0 Hz), 3.78 (1H, dd, J = 11.0, 4.0 Hz), 3.67 (1H, dd, J = 10.5, 4.5 Hz), 3.61 (1H, dd, J = 11.0, 7.0 Hz), 1.04 (9H, s), 1.01 (9H, s); ^{13}C NMR (75 MHz, CDCl_3) (only peaks for major regioisomer are listed) δ 162.0, 135.9, 135.9, 135.8, 135.7, 133.3, 133.3, 133.6, 133.2, 133.1, 130.1, 130.1, 130.0, 130.0, 129.2, 128.6, 128.0, 128.0, 127.9, 78.9, 66.9, 65.2, 64.7, 26.9, 26.9, 19.4, 19.4; IR (film) ν 3344, 3072, 2958, 2931, 2858, 2106, 1663, 1429, 1288, 1114, 1081, 824 cm^{-1} ; MS (DART) m/e (relative intensity): 793.2 (64, $(\text{M}^{(35}\text{Cl}_3)+\text{H})^+$), 632.3 (100), 589.3 (100), 351.2 (60), 316.1 (74), 233.1 (40); HRMS (DART): m/z calcd for $\text{C}_{40}\text{H}_{48}\text{Cl}_3\text{N}_4\text{O}_3\text{Si}_2$ ($\text{M}^{(35}\text{Cl}_3)+\text{H})^+$: 793.2330, found 793.2303.



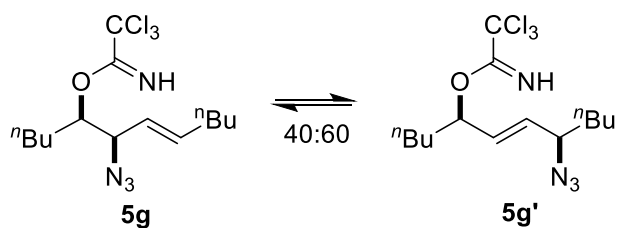
(5R*,6S*,E)-6-Azido-5-(2,2,2-trichloroacetoxy)dodec-7-ene (5d) and (5R*,8S*,E)-8-Azido-5-(2,2,2-trichloroacetoxy)dodec-6-ene (5d'): To a stirred solution of hydroxy allylic azides **4d** / **4d'** (0.183 g, 0.81 mmol) at 0 °C in CH₂Cl₂ (8 mL) was added DBU (0.18 mL, 1.22 mmol, 1.5 eq.), followed by dropwise addition of trichloroacetonitrile (0.15 mL, 1.47 mmol, 1.8 eq.). The solution was warmed to room temperature over 1.5 h, during which the solution turned orange-brown in colour. A solution of saturated ammonium chloride (10 mL) was added to the solution and the solution was extracted three times with dichloromethane. The combined organic layers were dried with MgSO₄ and the solution filtered through a short column of silica gel. The solvent was then evaporated in vacuo, and the crude mixture was purified by silica gel column chromatography (10:1, Hexanes: EtOAc) to afford pure allylic azides **5d** / **5d'** in a 30:70 ratio as a pale yellow oil (0.188 g, 63%), *R_f* = 0.65 and 0.70 (10:1 Hex: EtOAc). ¹H NMR (300 MHz, CDCl₃) 8.36 (0.3H, s, **d**), 8.30 (0.7H, s, **d'**), 5.84 (0.3H, dt, *J* = 15.0, 6.5 Hz, **d**), 5.66 – 5.77 (1.4H, m, **d'**), 5.49 (0.3H, dd, *J* = 15.0, 8.0 Hz, **d**), 5.36 – 5.44 (0.7H, m, **d'**), 5.08 (0.3H, dt, *J* = 9.0, 4.5 Hz, **d**), 4.15 (0.3H, dd, *J* = 8.0, 4.0 Hz, **d**), 3.79 – 3.88 (0.7 m, **d'**), 2.04 – 2.17 (1.4H, m **d'**), 1.23 – 1.87 (10.6H, d, *J* = 6.5 Hz, **d**), 0.86 – 0.94 (3H, m, **d** and **d'**); ¹³C NMR (100 MHz, CDCl₃) 162.6, 162.0, 138.7, 131.5, 131.2, 123.1, 79.8, 78.7, 66.2, 64.1, 34.3, 34.2, 32.2, 31.4, 29.8, 27.4, 27.3, 22.7, 22.6, 22.5, 22.3, 14.2, 14.1, 14.1 (missing 2 C); IR (film) ν 3347, 2958, 2933, 2862, 2100, 1662, 1291, 1076, 970 cm⁻¹; MS (DART) *m/e* (relative intensity): 534.3 (34), 437.2 (36), 321.2 (73), 180.2 (76), 97.1 (100); Molecular ion peak is not observed.



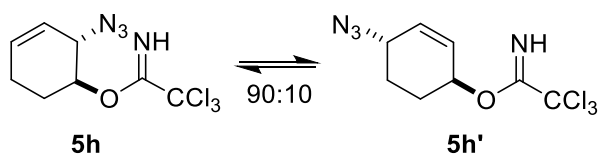
(4*R,5*R**,*E*)-4-Azido-1-(*tert*-butyldiphenylsilyloxy)-5-(2,2,2-trichloroacetoxy)hex-4-ene (5e) and (2*R**,5*S**,*E*)-2-Azido-1-(*tert*-butyldiphenylsilyloxy)-5-(2,2,2-trichloroacetoxy) hex-3-ene (5e')**: To a stirred solution of hydroxy allylic azides **4e** / **4e'** (0.207 g, 0.52 mmol) at 0 °C in CH₂Cl₂ (5 mL) was added DBU (0.12 mL, 0.78 mmol, 1.5 eq.), followed by dropwise addition of trichloroacetonitrile (94 μL, 0.94 mmol, 1.8 eq.). The solution was warmed to room temperature and stirred for 1 h, during which the solution turned orange in colour. A solution of saturated ammonium chloride (6 mL) was added to the solution and the solution was extracted with dichloromethane (3 x 5 mL). The combined organic layers were dried with MgSO₄ and the solution filtered through a short column of silica gel. The solvent was then evaporated in vacuo, and the crude product was purified by silica gel column chromatography (5:1, Hexanes: EtOAc) to afford pure allylic azides **5e** / **5e'** in a 40:60 ratio as a pale yellow oil (0.267 g, 95%), *R_f* = 0.25 and 0.30 (5:1 Hex/EtOAc). ¹H NMR (400 MHz, CDCl₃) δ 8.38 (0.4H, s, **e**), 8.31 (0.6H, s, **e'**), 7.65 – 7.68 (4H, m, **e** and **e'**), 7.36 – 7.46 (6H, m, **e** and **e'**), 5.90 – 5.97 (0.8H, m, **e**), 5.84 – 5.90 (0.6H, m, **e'**), 5.74 (0.6H, ddd, *J* = 15.5, 7.0, 1.0 Hz, **e'**), 5.50 (0.6H, dq, *J* = 6.5, 6.0 Hz, **e'**), 5.08 (0.4H, dq, *J* = 6.5, 6.0 Hz, **e**), 4.25 – 4.26 (0.8H, m, **e**), 4.10 (0.4H, dd, *J* = 6.5, 6.0 Hz, **e**), 4.00 (0.6H, dd, *J* = 6.5, 4.5 Hz, **e'**), 3.71 (0.6H, dd, *J* = 10.5, 4.5 Hz, **e'**), 3.66 (0.6H, dd, *J* = 10.5, 6.5 Hz, **e'**), 1.43 (1.8H, d, *J* = 6.4 Hz, **e'**), 1.34 (1.2H, d, *J* = 6.5 Hz, **e**), 1.06 (9H, s, **e** and **e'**); ¹³C NMR (75 MHz, CDCl₃) δ 162.2, 161.8, 135.9, 135.8, 135.7, 133.7, 133.2, 133.2, 130.1, 130.0, 128.0, 128.0, 126.6, 122.8, 76.6, 74.8, 66.7, 66.5, 64.6, 63.4, 27.0, 26.9, 19.8, 19.5, 19.4, 15.7 (missing 2 C); IR (film) ν 3343, 2932, 2858, 2105, 1663, 1277, 1113, 968 cm⁻¹; MS (DART) *m/e* (relative intensity): 556.1 (91), 463.1 (48), 370.2 (64), 275.1 (59); HRMS (DART): *m/z* calcd for C₂₄H₃₃Cl₃N₅O₂Si (M(³⁵Cl₃)+NH₄⁺): 556.1469, found 556.1471.



(2*R,3*S**,*E*)-3-Azido-1-(*tert*-butyldiphenylsilyloxy)-2-(2,2,2-trichloroacetoxy)hex-4-ene (5f) and (2*R**,5*S**,*E*)-5-Azido-1-(*tert*-butyldiphenylsilyloxy)-2-(2,2,2-trichloroacetoxy) hex-3-ene (5f')**: To a stirring solution of hydroxy allylic azides **4f** / **4f'** (0.304 g, 0.77 mmol) at 0 °C in CH₂Cl₂ (10 mL) was added DBU (0.135 mL, 1.38 mmol, 1.5 eq.), followed by dropwise addition of trichloroacetonitrile (0.170 mL, 1.15 mmol, 1.8 eq.). The solution was warmed to room temperature over 1.5 h, during which the solution turned orange in colour. A solution of saturated ammonium chloride (10 mL) was added to the solution and the solution was extracted with dichloromethane (3 x 10 mL). The combined organic layers were dried with MgSO₄ and the solution filtered through a short column of silica gel. The solvent was then evaporated in vacuo, and the crude was purified by silica gel column chromatography (10:1, Hexanes: EtOAc) to afford compound **5f** / **5f'** in a 15:85 ratio (5% of another isomer was identified as the *cis* isomer was also observed) as a colourless oil (0.278 g, 67%), *R_f* = 0.50 and 0.55 (15:1 hexanes: EtOAc). ¹H NMR (400 MHz, CDCl₃) (only peaks for major regioisomer are listed) δ 8.38 (1H, s), 7.64 – 7.75 (4H, m), 7.36 – 7.46 (6H, m), 5.70 – 5.84 (2H, m), 5.30 – 5.59 (1H, m), 3.78 – 4.02 (3H, m), 4.25 – 4.26 (2H, m), 3.83 (1H, dq, *J* = 7.0, 3.5 Hz), 1.26 (3H, d, *J* = 6.5 Hz), 1.04 (9H, s); ¹³C NMR (75 MHz, CDCl₃) (only peaks of major regioisomer are listed) δ 162.0, 135.9, 135.8, 133.3, 133.3, 130.0, 130.0, 128.0, 127.9, 127.8, 127.2, 78.8, 65.2, 58.8, 26.9, 20.0, 19.4 (missing 1 C); IR (film) ν 3339, 2931, 2858, 2103, 1663, 1293, 1113, 1079, 796, 701 cm⁻¹; MS (DART) *m/e* (relative intensity): 556.1 (59, (M(³⁵Cl₃)+H)⁺), 396.2 (35), 350.2 (98), 335.2 (100); HRMS (DART) calcd for C₂₄H₃₃Cl₃N₅O₂Si (M(³⁵Cl₃)+H)⁺ : 539.1203, found 539.1194.

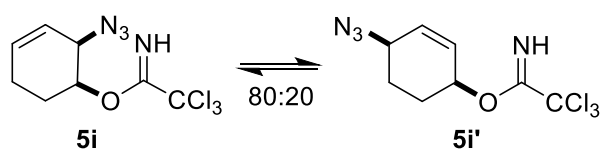


(5*R,6*R**,*E*)-6-Azido-5-(2,2,2-trichloroacetoxy)dodec-7-ene (5g) and (5*R**,8*R**,*E*)-8-Azido-5-(2,2,2-trichloroacetoxy)dodec-6-ene (5g')**: To a stirred solution of hydroxy allylic azides **4g** / **4g'** (67 mg, 0.297 mmol) at 0 °C in CH₂Cl₂ (4 mL) was added DBU (67 μL, 0.45 mmol, 1.5 eq.), followed by dropwise addition of trichloroacetonitrile (55 μL 0.54 mmol, 1.8 eq.). The solution was stirred at 0 °C for 1.5 h, during which the solution turned orange colour. A solution of saturated ammonium chloride (6 mL) was added to the solution and the solution was extracted with dichloromethane (3 x 5 mL). The combined organic layers were dried with MgSO₄ and the solution filtered through a short column of silica gel. The solvent was then evaporated in vacuo, and the crude was purified by silica gel column chromatography (10:1, Hexanes: EtOAc) to afford compound **5g** / **5g'** in a 60:40 ratio as colourless oil (76 mg, 70%). ¹H NMR (400 MHz, CDCl₃) δ 8.35 (0.4H, s, **g**), 8.31 (0.6H, s, **g'**), 5.78 – 5.86 (0.4H, m, **g**), 5.68 – 5.78 (1.2H, m, **g'**), 5.50 (0.6H, ddt, *J* = 15.0, 8.5, 1.5 Hz, **g**), 5.37 – 5.42 (0.6H, dq, m, **g'**), 5.05 (0.4H, dt, *J* = 7.0, 5.5 Hz, **g**), 4.08 (0.4H, dd, *J* = 8.5, 5.5 Hz, **g**), 3.80 – 3.90 (0.6, m, **g'**), 2.10 (1.2H, d, *J* = 7.0, 6.5 Hz, **g'**), 1.23 – 1.86 (10.8H, d, *J* = 6.5 Hz, **g**), 0.87 – 0.94 (3H, m, **g** and **g'**); ¹³C NMR (100 MHz, CDCl₃) δ 162.6, 161.9, 138.3, 131.5, 130.8, 123.3, 79.6, 78.4, 65.9, 64.0, 34.3, 34.2, 32.2, 31.3, 30.0, 28.1, 27.3, 27.2, 22.7, 22.6, 22.5, 22.3, 14.2, 14.1, 14.1 (missing 3 C); IR (film) ν 3348, 2958, 2931, 2862, 2100, 1662, 1276, 1076, 970, 750 cm⁻¹; MS (DART) *m/e* (relative intensity) 534.3 (59), 437.2 (62), 321.2 (36), 180.2 (100), 97.1 (62); Molecular ion peak is not observed.



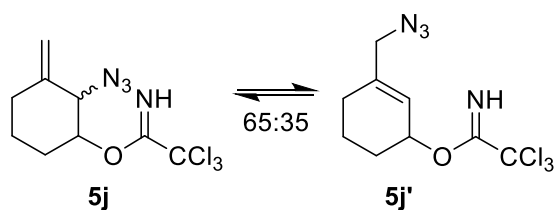
(1*S,2*S**)-2-Azido-1-(2,2,2-trichloroacetoxy) cyclohex-3-ene (5h) and (1*S**,4*S**)-4-Azido-1-(2,2,2-trichloroacetoxy) cyclohex-3-ene (5h')**: To a stirred solution of hydroxy allylic azides **4h** / **4h'** (400 mg, 2.88 mmol) at 0 °C in CH₂Cl₂ (40 mL) was added DBU (0.60 mL, 4.32 mmol), followed by dropwise addition of trichloroacetonitrile (0.52 mL 5.18 mmol). The solution was allowed to warm to room temperature over 1.5 – 2 h, during which the

solution turned orange in colour. A solution of saturated ammonium chloride (20 mL) was added to the solution and the solution was extracted CH₂Cl₂ (2 x 30 mL). The combined organic layers were dried with MgSO₄, filtered and then evaporated in vacuo. The crude mixture was purified by silica gel column chromatography (9:1 Hexanes: EtOAc) to afford pure compound **5h** / **5h'** in an 9:1 ratio as a colourless oil (680 mg, 84%), *R_f* = 0.50 and 0.55 (9:1 Hex/EtOAc).; ¹H NMR (400 MHz, CDCl₃) δ 8.43 (0.90H, s), 8.35 (0.10H, s), 6.09 – 6.13 (0.10H, m), 5.96 – 6.01 (0.90H, m), 5.59 – 5.64 (0.90H, m), 5.42 – 5.46 (0.10H, m), 5.07 (0.90H, ddd, *J* = 9.2, 6.2, 3.2 Hz), 5.01 (0.10H, ddd, *J* = 9.7, 6.5, 3.3 Hz), 4.10 – 4.13 (0.90H, m), 3.98 – 4.01 (0.10H, m), 2.18 – 2.29 (2H, m), 2.07 – 2.14 (0.10H, m), 1.83 – 1.92 (1H, m); ¹³C NMR (100 MHz, CDCl₃) δ 162.0, 161.8, 131.9, 130.1, 129.6, 122.8, 91.4, 77.1, 71.9, 59.6, 55.7, 25.8, 25.1, 24.1, 23.0 (missing 1C); IR (film) ν 3341, 2954, 2096, 1662, 1264, 1078, 796 cm⁻¹; HRMS (DART): *m/z* calcd for C₈H₁₀Cl₃N₄O [M + H]⁺ : 282.9920, found 282.9921.



(1*S,2*R**)-2-Azido-1-(2,2,2-trichloroacetoxy)cyclohex-3-ene (5i) and (1*S**,4*R**)-4-Azido-1-(2,2,2-trichloroacetoxy)cyclohex-3-ene (5i')**: To a stirred solution of hydroxy allylic azides **4i** / **4i'** (250 mg, 1.81 mmol) at 0 °C in CH₂Cl₂ (20 mL) was added DBU (0.38 mL, 2.71 mmol), followed by dropwise addition of trichloroacetonitrile (0.32 mL 3.26 mmol). The solution was allowed to warm to room temperature over 1.5 – 2 h, during which the solution turned orange in colour. A solution of saturated ammonium chloride (10 mL) was added to the solution and the solution was extracted CH₂Cl₂ (2 x 20 mL). The combined organic layers were dried with MgSO₄, filtered and then evaporated in vacuo. The crude mixture was purified by silica gel column chromatography to afford pure compound **5i** / **5i'** in an 80:20 ratio as a colourless oil (408 mg, 80%), *R_f* = 0.40 and 0.45 (10:1 Hex/EtOAc). ¹H NMR (400 MHz, CDCl₃) δ 8.40 (0.80H, s), 8.33 (0.20H, s), 6.11 – 6.15 (0.20H, m), 6.00 – 6.04 (0.80H, s), 5.96 – 5.98 (0.20H, m), 5.71 – 5.76 (0.80H, m), 5.34 – 5.37 (0.20H, m), 5.16 – 5.20 (0.80H, m), 4.24 – 4.26 (0.80H, m), 3.90 – 3.93 (0.20H, m), 2.16 – 2.36 (2H, m), 1.99 – 2.14 (1H, m), 1.90 – 1.95 (1H, m); ¹³C NMR (100 MHz, CDCl₃) δ 162.2, 132.8, 131.0, 128.9, 122.4, 76.3, 71.2, 56.9, 56.0, 24.9, 24.8, 23.9, 22.6 (missing 2 C); IR (film) ν 3341, 2954, 2096, 1662, 1264,

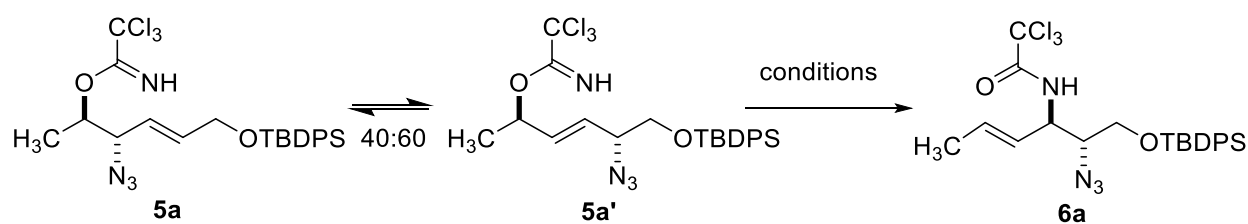
1078, 796 cm^{-1} ; HRMS (DART): m/z calcd for $\text{C}_8\text{H}_{10}\text{Cl}_3\text{N}_4\text{O}$ $[\text{M} + \text{H}]^+$: 282.9920, found 282.9911.



2-Azido-3-methylenecyclohexyl 2,2,2-trichloroacetimidate (5j) and 3-(azidomethyl)cyclohex-2-en-1-yl 2,2,2-trichloroacetimidate (5j'): To a stirred solution of hydroxy allylic azide **4j** / **4j'** (153 mg, 1.0 mmol) at 0 °C in CH_2Cl_2 (10 mL) was added DBU (0.23 mL, 1.5 mmol, 1.5 eq.), followed by dropwise addition of trichloroacetonitrile (0.18 mL 1.8 mmol, 1.8 eq.). The solution was warmed to room temperature over 1.5 h, during which the solution turned brown in colour. A solution of saturated ammonium chloride (15 mL) was added to the solution and the solution was extracted with dichloromethane (3 x 10 mL). The combined organic layers were dried with MgSO_4 and the solution filtered through a short column of silica gel. The solvent was then evaporated in vacuo, and the crude mixture was purified by silica gel column chromatography (5:1, Hexanes: EtOAc) to afford pure allylic azide **5j** / **5j'** in a 65:35 ratio as a colourless oil (82 mg, 27%), $R_f = 0.15$ and 0.25 (10:1 Hex: EtOAc). ^1H NMR (400 MHz, CDCl_3) δ 8.39 (0.65H, s, br, **j**), 8.29 (0.35H, s, br, **j'**), 5.92 – 5.95 (0.35H, m, **j'**), 5.42 – 5.49 (0.35H, m, **j'**), 5.02 – 5.13 (1.3H, m, **j**), 4.96 – 5.02 (0.33H, m, **j**), 4.85 (0.33H, ddd, $J = 8.0, 8.0, 4.0$ Hz, **j**), 4.50 (0.33H, d, $J = 3.5$ Hz, **j**), 4.15 (0.33H, d, $J = 8.0$ Hz, **j**) 3.70 – 3.80 (0.7H, m, **j'**), 1.39 – 2.42 (6H, m, **j** and **j'**); ^{13}C NMR (100 MHz, CDCl_3) δ 162.4, 162.1, 162.0, 143.1, 142.5, 139.5, 123.2, 114.3, 112.8, 79.2, 78.4, 72.9, 66.7, 66.3, 56.9, 32.6, 30.1, 27.8, 27.5, 26.8, 25.6, 23.7, 23.0, 18.9; IR (film) ν 3342, 2940, 2870, 2103, 1660, 1339, 1286, 1084, 796 cm^{-1} ; MS (DART) m/e (relative intensity): 404.1 (37), 349.1 (40), 288.2 (40), 261.2 (38), 188.1 (26), 153.1 (27), 126.1 (34), 108.1 (100); Molecular ion peak was not observed.

Microwave Assisted Domino Allylic Azide / Overman Rearrangements

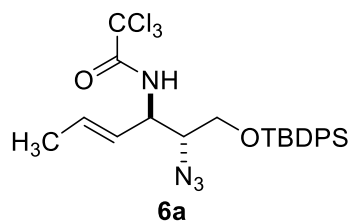
Table: Optimization of Microwave-Assisted Domino Rearrangement



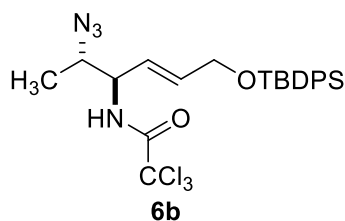
Entry	Conditions	T (°C) and time	Solvents	Results
1	Pd(CH ₃ CN) ₂ Cl ₂ (10%)	rt, 40 h	THF	No Reaction
2	Pd(PhCN) ₂ Cl ₂ (10%)	rt, 40 h	THF	No Reaction
3	Microwave, K ₂ CO ₃	140, 15 min	o-Xylenes	No Reaction
4	Microwave, K ₂ CO ₃	180, 15 min	DMF	Decomposition
5	Microwave, K ₂ CO ₃	165, 15 min	DMF	<10% conversion
6	Microwave, K ₂ CO ₃	165, 15 min	DME	50% conversion
7	Microwave, K ₂ CO ₃	165, 15 min	o-Dichlorobenzene	75% conversion
8	Microwave, K ₂ CO ₃	180, 15 min	o-Dichlorobenzene	>99% conversion

General Method for Microwave Domino Allylic Azide / Overman Rearrangement:

To a 5 mL dried microwave vial with a stir bar was added allylic trichloroacetimidate (0.12 mmol), o-dichlorobenzene (2 mL, 0.06 M), and K₂CO₃ (4 mg). The solution was stirred under a N₂ atmosphere for 5 min and then loaded into a microwave reactor (15 min, 180 °C, fixed time 'on'). After the reaction was finished, the solution was filtered through a short silica gel column using dichloromethane (2 x 10 mL), and the solution was evaporated in vacuo, and then with an air flow overnight to remove excess o-dichlorobenzene. The product was then purified by silica gel column chromatography to afford the pure allylic trichloroacetamide.

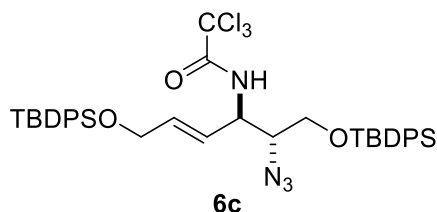


N-((2*R,3*R**,*E*)-2-Azido-1-((*tert*-butyldiphenylsilyl)oxy)hex-4-en-3-yl)-2,2,2-trichloroacetamide (**6a**):** The general procedure was used, followed by purification by silica gel chromatography (5:1, Hexanes: EtOAc) to give the product **6a** as a pale yellow oil (59.3 mg, 91%, $\geq 95:5$ dr), $R_f = 0.50$ (10:1 Hex/EtOAc). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.65 – 7.69 (4H, m), 7.36 – 7.48 (6H, m), 7.00 (1H, d, $J = 8.0$ Hz), 5.73 (1H, dqd, $J = 15.5, 6.5, 1.0$ Hz), 5.34 (1H, ddq, $J = 15.5, 7.5, 1.5$ Hz), 4.51 (1H, ddd, $J = 8.0, 7.5, 3.5$ Hz), 3.70 – 3.82 (3H, m), 1.58 (3H, dd, $J = 6.5, 1.5$ Hz), 1.08 (9H, s); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 161.2, 135.8, 132.7, 132.7, 132.2, 130.3, 130.2, 128.2, 128.1, 124.0, 65.3, 64.5, 54.0, 27.0, 19.3, 18.1 (missing 2 C); IR (film) ν 3334, 2929, 2857, 2101, 1707, 1505, 1111, 822, 703 cm^{-1} ; MS (EI) m/e (relative): 481.0 (9), 419.1 (9), 292.1 (51), 240.1 (68), 238.1 (44), 227.1 (28), 197.1 (61), 181.0 (92), 162.0 (86), 135.1 (100), 105.0 (70), 57.1 (97); HRMS (EI): m/z calcd for $\text{C}_{20}\text{H}_{20}\text{N}_4\text{O}_2\text{SiCl}_3$ ($-\text{C}_4\text{H}_9$): 481.0413, found 481.0421.

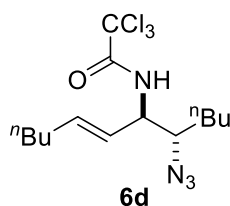


N-((2*S,3*R**,*E*)-2-Azido-6-((*tert*-butyldiphenylsilyl)oxy)hex-4-en-3-yl)-2,2,2-trichloroacetamide (**6b**):** The general procedure was used, followed by purification by silica gel chromatography (15:1 hexanes: EtOAc) to give the product **6b** as a colourless oil (46.6 mg, 70%, $\geq 95:5$ dr), $R_f = 0.45$ (15:1, Hexanes : EtOAc). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.65 – 7.69 (4H, m), 7.36 – 7.43 (6H, m), 6.90 (1H, d, $J = 8.0$ Hz), 5.87 (1H, dt, $J = 15.5, 3.5$ Hz), 5.78 (1H, ddt, $J = 15.5, 6.0, 1.5$ Hz), 3.98 – 4.45 (1H, m), 4.25 – 4.26 (2H, m), 3.83 (1H, dq, $J = 7.0, 3.5$ Hz), 1.30 (3H, d, $J = 7.0$ Hz), 1.07 (9H, s); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 161.2, 135.7, 135.7, 133.6, 133.6, 130.0, 130.0, 128.0, 122.0, 63.6, 59.7, 56.9, 27.0, 19.5, 16.0 (missing 3 C); IR (film) ν 3413, 3337, 2931, 2857, 2118, 1713, 1507, 1260, 1113, 822, 701

cm⁻¹; MS DART (relative intensity): 556.1 (59, M(³⁵Cl₃)+NH₄⁺), 463.1 (41), 283.0 (100); HRMS (EI): *m/z* calcd for C₂₄H₃₃Cl₃N₅O₂Si (M(³⁵Cl₃)+NH₄⁺): 556.1469, found 556.1469.

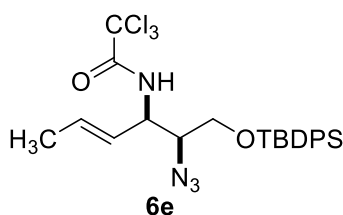


***N*-((4*S**,5*R**,*E*)-5-Azido-1,6-di(*tert*-butyldiphenylsilyloxy)hex-2-en-4-yl)-2,2,2-trichloroacetamide (6c):** The general procedure was used, followed by purification by silica gel chromatography (20:1 hexanes: EtOAc) to give the product **6c** as a colourless oil (96 mg, 62%, $\geq 95:5$ dr), *R_f* = 0.55 (20:1, Hexanes: EtOAc). ¹H NMR (400 MHz, CDCl₃) δ 7.60 – 7.68 (8H, m), 7.31 – 7.43 (12H, m), 7.02 (1H, d, *J* = 8.5 Hz), 5.79 (1H, dddd, *J* = 15.5, 4.0, 4.0, 0.5 Hz), 5.70 (1H, ddt, *J* = 15.5, 7.0, 1.5 Hz), 4.58 – 4.62 (1H, m), 4.15 – 4.17 (2H, m), 3.71 – 3.82 (3H, m), 1.08 (9H, s), 1.04 (9H, s); ¹³C NMR (100 MHz, CDCl₃) δ 161.3, 135.8, 135.8, 135.7, 135.7, 135.0, 133.6, 133.5, 132.7, 132.7, 130.3, 130.3, 130.0, 128.2, 128.0, 122.4, 65.4, 64.6, 63.5, 53.4, 27.0, 27.0, 19.5, 19.4. (missing 3 C); IR (film) ν 3408, 3342, 3071, 2931, 2858, 2105, 1720, 1503, 1428, 1264, 1113, 823, 701 cm⁻¹; MS DART (relative intensity): 810.3 (44, M(³⁵Cl₃)+NH₄⁺), 537.1 (97); HRMS (EI): *m/z* calcd for C₄₀H₅₁Cl₃N₅O₃Si₂ (M(³⁵Cl₃)+H)⁺: 810.2596, found 810.2574.

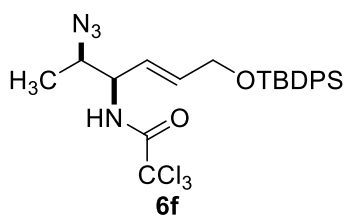


***N*-((7*R**,8*S**,*E*)-8-Azidododec-5-en-7-yl)-2,2,2-trichloroacetamide (6d):** The general procedure was used, followed by purification by silica gel chromatography (10:1 hexanes: EtOAc) to give the product **6d** as a colourless oil (46.8 mg, 91%, $\geq 95:5$ dr), *R_f* = 0.6 (15:1 hexanes: EtOAc). ¹H NMR (300 MHz, CDCl₃) δ 6.92 (1H, d, *J* = 8.0 Hz), 5.81 (1H, dtd, *J* = 15.5, 6.5, 1.0 Hz), 5.40 (1H, ddt, *J* = 15.5, 8.0, 1.5 Hz), 4.41 (1H, ddd, *J* = 8.0, 8.0, 3.5 Hz), 3.57-3.61 (1H, m), 2.05 – 2.12 (3H, m), 1.25 – 1.65 (10H, m), 0.93 (3H, t, *J* = 7.0 Hz), 0.90 (3H, t, *J* = 7.0 Hz); ¹³C NMR (75 MHz, CDCl₃) δ 161.9, 138.2, 122.3, 64.8, 56.7, 32.3, 31.1, 31.1, 28.3, 22.6, 22.3, 14.1, 14.1 (missing 1 C); IR (film) ν 3332, 2958, 2931, 2101, 1705,

1510, 1262, 821 cm^{-1} ; MS DART+ (relative intensity): 386.1 (58, $\text{M}^{(35}\text{Cl}_3)+\text{NH}_4^+$), 369.1 (90, $\text{M}^{(35}\text{Cl}_3)+\text{H}^+$), 341.1 (100); HRMS (EI): m/z calcd for $\text{C}_{14}\text{H}_{24}\text{Cl}_3\text{N}_4\text{O}$ ($\text{M}^{(35}\text{Cl}_3)+\text{H}^+$): 369.1015, found 369.1008.

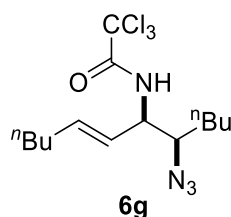


***N*-((2*S**,3*R**,*E*)-2-Azido-1-(*tert*-butyldiphenylsilyloxy)hex-4-en-3-yl)-2,2,2-trichloroacetamide (6e):** The general procedure was used, followed by purification by silica gel chromatography (5:1 hexanes: EtOAc) to give the product **6e** as a pale yellow oil (58.0 mg, 89%, $\geq 95:5$ dr), $R_f = 0.40$ (10:1 Hex/EtOAc). ^1H NMR (300 MHz, CDCl_3) δ 7.61 – 7.69 (4H, m), 7.35 – 7.47 (6H, m), 6.77 (1H, d, $J = 9.0$ Hz), 5.74 (1H, dq, $J = 15.5, 6.5$ Hz), 5.44 (1H, dd, $J = 15.5, 6.5$ Hz), 4.48 – 4.54 (1H, dd, m), 3.62– 3.79 (3H, m), 1.72 (3H, d, $J = 6.5$ Hz), 1.08 (9H, s); ^{13}C NMR (75 MHz, CDCl_3) δ 161.4, 135.8, 133.6, 132.7, 130.2, 130.0, 129.1, 128.1, 128.1, 128.0, 126.8, 66.6, 64.6, 52.8, 27.0, 19.3, 18.1 (missing 1 C); IR (film) ν 3343, 2932, 2859, 2104, 1663, 1287, 1113, 1080, 797, 702 cm^{-1} ; MS DART m/e (relative intensity): 556.1 (90), 461.01 (37), 370.2 (64), 275.1 (58); HRMS (DART): m/z calcd for $\text{C}_{24}\text{H}_{33}\text{Cl}_3\text{N}_5\text{O}_2\text{Si}$ ($\text{M}^{(35}\text{Cl}_3)+\text{NH}_4^+$): 556.1469, found 556.1471.

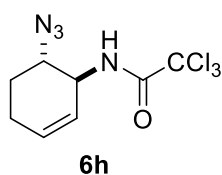


***N*-((4*R**,5*R**,*E*)-5-Azido-1-(*tert*-butyldiphenylsilyloxy)hex-2-en-4-yl)-2,2,2-trichloroacetamide (6f):** The general procedure was used, followed by purification by silica gel chromatography (15:1 hexanes: EtOAc) to give the product **6f** as a colourless oil (38.9 mg, 60%, $\geq 95:5$ dr), $R_f = 0.45$ (15:1 hexanes : EtOAc). ^1H NMR (300 MHz, CDCl_3) δ 7.64 – 7.68 (4H, m), 7.35 – 7.43 (6H, m), 6.75 (1H, d, $J = 9.0$ Hz), 5.80 – 5.82 (2H, m), 4.45 – 4.51 (1H, m), 4.23 – 4.24 (2H, m), 3.83 (1H, dq, $J = 6.5, 3.0$ Hz), 1.34 (3H, d, $J = 6.5$ Hz), 1.07 (9H, s); ^{13}C NMR (75 MHz, CDCl_3) δ 161.9, 135.7, 133.6, 133.6, 130.0, 128.0, 128.0, 125.5, 63.6, 60.9, 56.4, 27.0, 19.5, 17.0 (missing 3 C); IR (film) ν 3412, 3340, 2931, 2857, 2122, 1715,

1262, 1113, 822, 702 cm^{-1} ; MS DART+ (relative intensity): 556.1 (68, $(\text{M}^{(35}\text{Cl}_3)+\text{NH}_4^+)$), 461.1 (98), 283.0 (51); HRMS (DART): m/z calcd for $\text{C}_{24}\text{H}_{33}\text{Cl}_3\text{N}_5\text{O}_2\text{Si}$ ($\text{M}^{(35}\text{Cl}_3)+\text{NH}_4^+$): 556.1469, found 556.1463.

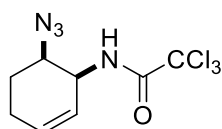


***N*-((7*R**,8*R**,*E*)-8-Azidododec-5-en-7-yl)-2,2,2-trichloroacetamide (6g):** The general procedure was used, followed by purification by silica gel chromatography (15:1, Hexanes: EtOAc) to give the product **6g** as a white crystalline solid (0.317 g, 71%, $\geq 95:5$ dr), $R_f = 0.6$ (15:1 hexanes : EtOAc), mp = 38-40 °C. ^1H NMR (400 MHz, CDCl_3) δ 6.92 (1H, d, $J = 8.0$ Hz), 5.81 (1H, dtd, $J = 15.5, 6.5, 1.0$ Hz), 5.40 (1H, dtd, $J = 15.5, 8.0, 1.5$ Hz), 4.41 (1H, ddd, $J = 8.0, 8.0, 3.5$ Hz), 3.57 – 3.61 (1H, m), 2.05 – 2.12 (3H, m), 1.25 – 1.65 (10H, m), 0.93 (3H, t, $J = 7.0$ Hz), 0.90 (3H, t, $J = 7.0$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 161.7, 135.3, 125.7, 66.7, 55.6, 32.2, 31.8, 31.2, 28.5, 22.6, 22.4, 14.1, 14.1 (missing 1 C); IR (film) ν 3330, 2958, 2930, 2100, 1704, 1513, 1261, 821, 750 cm^{-1} ; MS DART+ (relative intensity): 386.1 (45, $\text{M}^{(35}\text{Cl}_3)+\text{NH}_4^+$), 369.1 (100, $\text{M}^{(35}\text{Cl}_3)+\text{H}^+$), 341.1 (83); HRMS (DART): m/z calcd for $\text{C}_{14}\text{H}_{24}\text{Cl}_3\text{N}_4\text{O}$ ($\text{M}^{(35}\text{Cl}_3)+\text{H}^+$): 369.1015, found 369.1020.



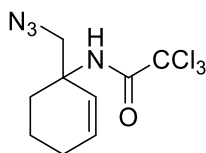
***N*-((1*S**,6*S**)-6-Azidocyclohex-2-en-1-yl)-2,2,2-trichloroacetamide (6h):** To a solution of allylic trichloroacetimidate **5h** / **5h'** (400 mg, 1.42 mmol) in 20 mL microwave vial with a stir bar was added *o*-dichlorobenzene (10 mL), and K_2CO_3 (30 mg). The resulting solution was stirred under a N_2 atmosphere for 5 min and then loaded into a microwave reactor (15 min, 180 °C, fixed time 'on'). After completion of reaction, the solution was filtered through a short silica gel column using CH_2Cl_2 (2 x 20 mL), and the solution was evaporated in vacuo, and then with an air flow overnight to remove excess *o*-dichlorobenzene. The product was then purified by silica gel chromatography (5:1 Hexanes: EtOAc) to give the product **6h** as a white solid (335 mg, 84%, $\geq 95:5$ dr), $R_f = 0.30$ (10:1 Hexanes/EtOAc), mp = 73-74 °C, ^1H NMR

(400 MHz, CDCl₃) δ 6.57 (1H, br, s), 5.94 – 5.99 (1H, m), 5.54 – 5.58 (1H, m), 4.38 – 4.43 (1H, m), 3.65 (1H, ddd, J = 10.0, 7.0, 3.0 Hz), 2.14 – 2.33 (2H, m), 1.98 – 2.05 (1H, m), 1.82 – 1.92 (1H, m); ¹³C NMR (100 MHz, CDCl₃) δ 161.7, 131.7, 124.0, 92.5, 60.3, 51.9, 25.4, 23.2; IR (film) ν 3335, 2931, 2106, 1715, 1507, 820 cm⁻¹; HRMS (DART): m/z calcd for C₈H₁₀Cl₃N₄O [M + H]⁺ : 282.9920, found 282.9928.



6i

N-((1S*,6R*)-6-Azidocyclohex-enyl)-2,2,2-trichloroacetamide (6i): To a solution of allylic trichloroacetimidate **5i** / **5i'** (350 mg, 1.24 mmol) in a 20 mL microwave vial with a stir bar was added o-dichlorobenzene (10 mL), and K₂CO₃ (25 mg). The resulting solution was stirred under a N₂ atmosphere for 5 min and then loaded into a microwave reactor (15 min, 180 °C, fixed time 'on'). After completion of reaction, the solution was filtered through a short silica gel column using CH₂Cl₂ (2 x 20 mL), and the solution was evaporated in vacuo, and then with an air flow overnight to remove excess o-dichlorobenzene. The product was then purified by silica gel chromatography (5:1 Hexanes: EtOAc) to give the product **6i** as a white solid (308 mg, 90%, \geq 95:5 dr), R_f = 0.30 (10:1, Hexanes/EtOAc), mp = 50-53 °C. ¹H NMR (400 MHz, CDCl₃) δ 6.86 (1H, s), 5.92 – 5.97 (1H, m), 5.45 – 5.49 (1H, m), 4.63 – 4.69 (1H, m), 4.07 – 4.10 (1H, m), 2.22 – 2.33 (1H, m), 2.00 – 2.16 (2H, m), 1.92 – 1.97 (1H, m); ¹³C NMR (100 MHz, CDCl₃) δ 161.7, 131.2, 123.7, 92.5, 58.3, 49.2, 24.6, 21.1; IR (film) ν 3341, 2954, 2096, 1662, 796 cm⁻¹; HRMS (DART): m/z calcd for C₈H₁₀Cl₃N₄O [M + H]⁺ : 282.9920, found 282.9928.



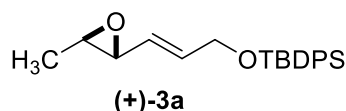
6j

N-(1-(Azidomethyl)cyclohex-2-enyl)-2,2,2-trichloroacetamide (6j): The general procedure was used, followed by purification by silica gel chromatography (5:1 hexanes: EtOAc) to give the product **6j** as white crystalline solid (58%, \geq 95:5 dr), R_f = 0.40 (10:1 Hex/EtOAc), mp = 39-40 °C. ¹H NMR (400 MHz, CDCl₃) δ 6.51 (1H, s), 6.04 (1H, m), 5.87 (1H, m), 3.91 (1H, d, J = 12.5 Hz), 3.59 (2H, d, J = 12.5 Hz), 2.02 – 2.26 (m, 3H), 1.61 – 1.78 (m, 3H); ¹³C NMR

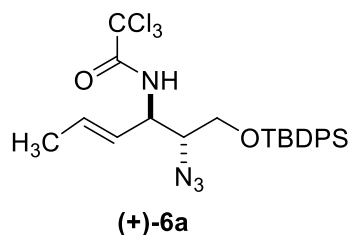
(100 MHz, CDCl₃) δ 160.8, 133.9, 126.1, 56.9, 56.0, 29.8, 25.2, 18.4 (missing 1C); IR (film) ν 3420, 2930, 2103, 1718, 1502, 1268, 820 cm⁻¹; HRMS (DART): m/z calcd for C₉H₁₁N₄ONaCl₃ (M(³⁵Cl₃)+Na⁺): 318.9890, found 318.9878.

Rearrangement with Enantioenriched Substrate:

An enantiomerically pure vinyl epoxide (+)-**3a** could be obtained in one step from the Shi epoxidation in 95% ee. After ring opening on (+)-**3a** with azide followed by formation of trichloroacetimidate and domino rearrangement, the enantiomeric excess of the final compound (+)-**6a** was determined to be 87% by chiral column HPLC, which shows minimal loss of chirality from the starting chiral vinyl epoxide (+)-**3a**.

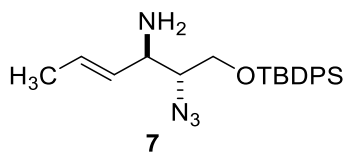


tert-Butyl(((E)-3-((2R,3R)-3-methyloxiran-2-yl)allyl)oxy)diphenylsilane ((+)-3a**):** To a stirred solution of aqueous EDTA (50 mL, 4 x 10⁻⁴ M) in a 3-necked 1 L round bottom flask was added Na₂B₂O₇·10H₂O (0.955 g, 2.50 mmol). Dimethoxymethane (50 mL) was then added, followed by the addition of the TBDPS protected sorbic alcohol (1.683 g, 5.00 mmol) in acetonitrile (25 mL), and then followed by tetra butyl ammonium hydrogen sulphate (0.075 g, 0.20 mmol). Shi epoxidation diketal catalyst (0.3244 g, 1.25 mmol, 0.25 eq.) was added to the solution and the solution was cooled to 0 °C (ice-water bath). Oxone (3.448 g, 6 mmol, 1.2 eq.) in aqueous EDTA (30 mL) and K₂CO₃ (3.45 g) in water (30 mL) was added separately via syringe pump over 1.5 h. After addition was complete, hexanes (30 mL) was added to the solution and the solution was extracted with hexanes (3 x 20 mL). The combined organic layers were dried with addition of anhydrous MgSO₄, filtered, and evaporated to give the regioisomeric epoxides (+)-**3a** and (+)-**3b** in a 4.5: 1 ratio. The isomers were then separated by column chromatography to give (+)-**3a** in 63% yield which solidified upon storage in a fridge as a white solid. ¹H-NMR, ¹³CNMR, IR and HRMS data were identical with the racemic form for both compounds. mp = 28-29 °C. The optical purity was determined by chiral HPLC (25 cm Chiralcel AD-H column with eluent 99.8:0.2 Hexanes: isopropanol at 1 mL/min, (R,R) isomer = 12.8 min, (S,S) isomer = 14.5 min); (95% ee): [α]_D²⁵ = +15.7° (c = 1.00 in CHCl₃).

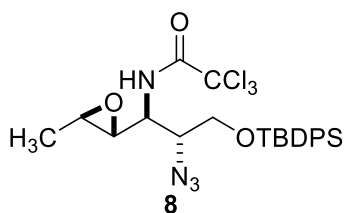


N-((2*R*,3*R*,*E*)-2-Azido-1-((*tert*-butyldiphenylsilyloxy)hex-4-en-3-yl)-2,2,2-trichloroacetamide ((+)-6a): The general procedure was used, followed by purification by silica gel chromatography (5:1 hexanes: EtOAc) to give the product (+)-6a as a beige crystalline solid (62 mg, 90%), mp = 73-75 °C. ¹H-NMR, ¹³C-NMR, IR and HRMS data were identical with the racemic form. The optical purity was determined by chiral HPLC (25 cm Chiralcel AD-H column with eluent 98:2.0 hexanes: isopropanol at 1.0 mL/min (*R*, *R*) isomer = 11.2 min, (*S*, *S*) isomer = 5.3 min); (*R*,*R*) isomer (89% ee): $[\alpha]^{25} = +19.3$ (*c* = 1.0 in CHCl₃).

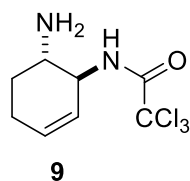
Representative derivatizations:



(2*R,3*S**,*E*)-3-Amino-2-azido-1-((*tert*-butyldiphenylsilyloxy)hex-4-ene (7):** To a solution of allylic trichloroacetamide 6a (0.216 g, 0.40 mmol) in toluene (10 mL, 0.25 M) at -78 °C (dry ice / acetone) was added 1.0 M DIBAL-H in hexanes (2.0 mL, 5.0 eq.) and the reaction was stirred at -78 °C for 15 min. Ice-cold acetone (1 mL) was then added, followed by addition of Na₂SO₄, and the reaction was stirred for another 1 hour. The mixture was then filtered through a pad of celite and washed with CH₂Cl₂ (15 mL). The filtrate was evaporated and purified by silica gel flash chromatography (4:1 Hexanes: EtOAc with 5% Et₃N) to afford compound 7 (114 mg, 72%) as a pale yellow oil. *R_f* = 0.15 (2:1 Hexanes: EtOAc, 5% Et₃N); ¹H NMR (400 MHz, CDCl₃) δ 7.66 – 7.70 (4H, m), 7.39 – 7.45 (6H, m), 5.55 (1H, dqd, *J* = 15.0, 6.5, 1.0 Hz), 5.34 (1H, ddq, *J* = 15.5, 7.5, 1.5 Hz), 3.74 – 3.78 (1H, m), 3.45 – 3.50 (1H, m), 3.40 (1H, dd, *J* = 7.5, 5.0 Hz), 1.58 (3H, dd, *J* = 6.5, 1.0 Hz), 1.30 (2H, s, br); 1.07 (9H, s); ¹³C NMR (75 MHz, CDCl₃) δ 135.8, 135.8, 133.2, 131.3, 130.1, 128.1, 128.0, 128.0, 68.8, 64.8, 54.4, 26.7, 19.4, 18.0 (missing 2 C); IR (film) ν 3334 (weak), 2932, 2857, 2100, 1428, 1111, 822, 703 cm⁻¹; HRMS (EI): *m/z* calcd for C₂₂H₃₁N₄O_{Si}: 395.2261, found 395.2255.

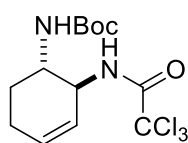


***N*-((1*S**,2*R**)-2-Azido-3-((*tert*-butyldiphenylsilyloxy)-1-((2*R*,3*R*)-3-methyloxiran-2-yl)propyl)-2,2,2-trichloroacetamide (**8**):** To a solution of allylic trichloroacetamide **6a** (0.163 g, 0.30 mmol) in CH₂Cl₂ (3 mL, 1.0 M) at 0 °C (ice bath) was added *m*CPBA (80 mg, 0.36 mmol, 1.2 eq.). The reaction was allowed warm to room temperature and stirred for 24 h. A saturated solution of Na₂SO₃ was then added and the aqueous layer was extracted once with CH₂Cl₂. The organic layer was then washed with saturated solution of NaHCO₃ (5 mL), followed with saturated brine (5 mL). The organic layer was then dried with MgSO₄, filtered, and evaporated and purified by silica gel column chromatography to give epoxide **8** in a 88:12 diastereomer ratio (0.146 g, 87%) as a white solid, mp = 99-102 °C, *R*_f = 0.45 (8:1 Hexanes: EtOAc); ¹H NMR (400 MHz, CDCl₃) δ 7.65 – 7.70 (4H, m), 7.37 – 7.45 (6H, m), 6.75 (1H, d, *J* = 9.0 Hz), 4.19 (1H, ddd, *J* = 9.0, 6.5, 2.0 Hz), 3.77 – 3.90 (3H, m) 3.02 (1H, dd, *J* = 2.0, 2.0 Hz), 2.81 (1H, qd, *J* = 2.0, 5.5 Hz), 1.58 (3H, d, *J* = 5.5 Hz), 1.09 (9H, s); ¹³C NMR (100 MHz, CDCl₃) δ 162.0, 135.8, 132.7, 132.6, 130.3, 130.3, 128.2, 128.2, 128.2, 64.8, 64.6, 56.5, 51.9, 50.0, 27.1, 27.0, 26.9, 19.3, 17.0; IR (film) ν 3333, 2932, 2859, 2102, 1716, 1513, 1264, 1114, 822, 701 cm⁻¹; HRMS (DART): *m/z* calcd for C₂₄H₃₀Cl₃N₄O₃Si (M(³⁵Cl₃)+H)⁺: 555.1152, found 555.1134.



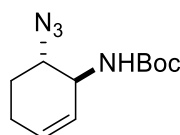
***N*-((1*S**,6*S**)-6-Aminocyclohex-2-en-1-yl)-2,2,2-trichloroacetamide (**9**):** To a solution of azide **6h** (50 mg, 179 μmol) in THF/water (5 mL of 4:1 v/v mixture) was added polymer-bound triphenylphosphine (89 mg of 3 mmol/g resin, 267 μmol) at room temperature and the resulting suspension was stirred at 65 °C for 24 h. The reaction mixture was then cooled to room temperature and filtered through a short pad of Celite and washed with CH₂Cl₂ (2 x 10 mL). The combined filtrates were concentrated under reduced pressure and the residue dissolved in CH₂Cl₂ (20 mL). The resulting solution was washed with water (10 mL) and dried over MgSO₄, filtered and concentrated under reduced pressure to give a yellow oil. The crude product was then purified by silica gel chromatography (9:1, CH₂Cl₂: MeOH) to give the

product **9** as white solid (33 mg, 73%), $R_f = 0.40$ (9:1 CH_2Cl_2 : MeOH), mp = 76-78 °C. ^1H NMR (400 MHz, CDCl_3) δ 6.68 (1H, d, $J = 7.8$ Hz), 5.89 – 5.93 (1H, m), 5.51 – 5.55 (1H, m), 4.24 – 4.29 (1H, m), 2.95 (1H, td, $J = 10.3, 3.0$ Hz) 2.16 – 2.21 (2H, m), 2.10 (2H, br. s), 1.89 – 1.96 (1H, m), 1.62 – 1.72 (1H, m); ^{13}C NMR (100 MHz, CDCl_3) δ 162.4, 131.6, 124.9, 92.8, 55.8, 52.0, 29.5, 24.0; IR (film) ν 3392, 3310, 2919, 1682, 820 cm^{-1} ; HRMS (DART): m/z calcd for $\text{C}_8\text{H}_{12}\text{Cl}_3\text{N}_2\text{O}$ $[\text{M} + \text{H}]^+$: 257.0015, found 257.0022.



10

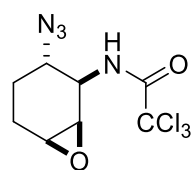
tert-Butyl ((1S*,2S*)-2-(2,2,2-trichloroacetamido) cyclohex-3-en-1-yl) carbamate (10): To a solution of **9** (25 mg, 0.104 mmol) in CH_2Cl_2 (5 mL) at 0 °C was added Et_3N (29 μL , 0.208 mmol), followed by dropwise addition of di-*tert*-butyl dicarbonate (Boc_2O , 34 μL , 0.156 mmol). The reaction mixture was warmed to room temperature and was stirred for an additional 12 h. The solvent was then evaporated in vacuo, and the crude mixture was purified by silica gel column chromatography (1:1 Hexane: EtOAc) to afford compound **10** as white solid (33 mg, 95%), $R_f = 0.50$ (1:1 Hexane/EtOAc), mp = 85-87 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.62 (1H, d, $J = 8.2$ Hz), 5.79 – 5.81 (1H, m), 5.59 – 5.62 (1H, m), 4.71 (1H, d, $J = 8.2$ Hz), 4.26 – 4.30 (1H, m), 3.71 – 3.79 (1H, m), 2.16 – 2.29 (2H, m), 1.97 – 2.01 (1H, m), 1.63 – 1.72 (1H, m), 1.42 (9H, s); ^{13}C NMR (100 MHz, CDCl_3) δ 162.8, 156.6, 129.5, 125.9, 92.6, 80.4, 56.3, 50.6, 28.5, 28.5, 25.4; IR (film) ν 3310, 1662, 1163, 819 cm^{-1} ; HRMS (DART): m/z calcd for $\text{C}_{13}\text{H}_{20}\text{Cl}_3\text{N}_2\text{O}_3$ $[\text{M} + \text{H}]^+$: 357.0539, found 357.0549.



12

tert-Butyl ((1S*,6S*)-6-azidocyclohex-2-en-1-yl) carbamate (12): To a magnetically stirred solution of trichloroacetamide **6h** (60 mg, 0.212 mmol) in anhydrous toluene (10 mL) at –78 °C was added DIBAL-H (1.06 mL of a 1 M solution in toluene, 1.06 mmol). The resulting solution was stirred at this temperature for 30 min and then treated with ice-cold acetone (10

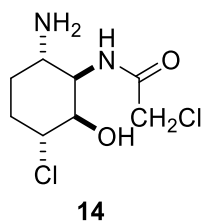
mL), followed by Na₂SO₄·10H₂O (682 mg, 2.12 mmol). The reaction mixture was allowed to warm to room temperature and stirred for 1 h. The resulting solids were filtered off using a pad consisting of a layer of Celite and washed with CH₂Cl₂ (2 X 15 mL). The solvent was then evaporated in vacuo, and the crude product **11** was dissolved in CH₂Cl₂ (8 mL) and then Et₃N (60 μL, 0.425 mmol) was added, followed by dropwise addition of di-*tert*-butyl dicarbonate (Boc₂O, 70 μL, 0.319 mmol) at 0 °C. The reaction mixture was then warmed to room temperature and was stirred an additional 3 h. The solvent was then evaporated in vacuo, and the crude was purified by silica gel column chromatography (8:2 Hexane: EtOAc) to afford compound **12** as white solid (38 mg 76%), R_f = 0.5 (8:2 Hexane/EtOAc), mp = 56-58 °C. ¹H NMR (400 MHz, CDCl₃) δ 5.79 – 5.83 (1H, m), 5.49 – 5.54 (1H, m), 4.58 (1H, s), 4.09 (1H, s), 3.51 – 3.55 (1H, m), 2.03 – 2.23 (2H, m), 1.88 – 1.95 (1H, m), 1.71 – 1.80 (1H, m), 1.45 (9H, s); ¹³C NMR (100 MHz, CDCl₃) δ 155.2, 130.0, 126.1, 80.0, 61.3, 50.9, 28.5, 25.2, 23.0; IR (film) ν 3018, 2097, 1705, 1215 cm⁻¹; HRMS (DART): *m/z* calcd for C₁₁H₁₉N₄O₂ [M + H]⁺: 239.1508, found 239.1505.



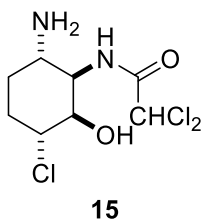
13

***N*-((1*R**,2*R**,3*S**,6*S**)-3-Azido-7-oxabicyclo[4.1.0]heptan-2-yl)-2,2,2-trichloroacetamide (**13**)** : To a solution of allylic trichloroacetamide **6h** (100 mg, 0.354 mmol) in CH₂Cl₂ (10 mL) at 0 °C was added *m*CPBA (77%) (94 mg, 0.424 mmol). The reaction was allowed warm to room temperature and stirred for 24 h. A saturated solution of Na₂SO₃ was then added and the aqueous layer was extracted with CH₂Cl₂ (20 mL). The organic layer was then washed with saturated solution of NaHCO₃ (10 mL), followed with saturated brine (10 mL). The organic layer was then dried with MgSO₄, filtered, evaporated and was purified by flash chromatography (5:1, Hexanes: EtOAc) to give epoxide **13** as a white solid (96 mg, 91%), mp = 130-132 °C. R_f = 0.30 (5:1 Hexanes: EtOAc). ¹H NMR (400 MHz, CDCl₃) δ 7.03 (1H, d, *J* = 8.5 Hz), 4.26 (1H, dt, *J* = 8.4, 4.5 Hz), 3.54 – 3.58 (1H, m), 3.40 – 3.42 (1H, m), 3.36 (1H, t, *J* = 3.8 Hz), 2.10 – 2.16 (2H, m), 1.71 – 1.79 (1H, m), 1.57 – 1.65 (1H, m); ¹³C NMR (100 MHz, CDCl₃) δ 161.9, 92.30, 57.6, 54.3, 52.4, 50.5, 22.0, 20.3; IR (film) ν 3352, 2927, 2096, 863 cm⁻¹; HRMS (DART): *m/z* calcd for C₈H₁₀Cl₃N₄O₂ [M + H]⁺ : 298.9870, found 298.9869.

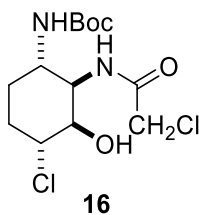
***N*-((1*R**,2*R**,3*R**,6*S**)-6-Amino-3-chloro-2-hydroxycyclohexyl)-2-chloroacetamide (14) and *N*-((1*R**,2*R**,3*R**,6*S**)-6-Amino-3-chloro-2-hydroxycyclohexyl)-2,2-dichloroacetamide (15):** A stirred solution of **13** (60 mg, 0.201 mmol) in MeOH/EtOAc (1:2, v/v) mixture (6 mL) was hydrogenated over 5% Pd/C (~10 mg) for 3 h. Subsequently, the solution was passed through Celite and washed with MeOH (10 mL). The combined filtrates were concentrated under reduced pressure and the crude product was then purified by silica gel chromatography (9:1 to 8:2 CH₂Cl₂: MeOH) to give the two products **14** and **15** as white solids in a 3:1 ratio.



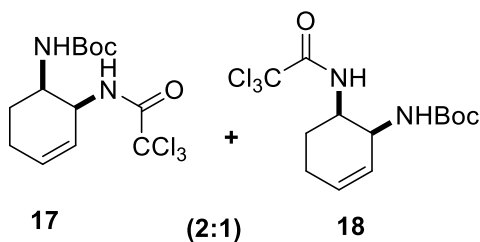
***N*-((1*R**,2*R**,3*R**,6*S**)-6-Amino-3-chloro-2-hydroxycyclohexyl)-2-chloroacetamide (14):** White solid (34 mg, 70%), $R_f = 0.30$ (8:2 CH₂Cl₂/MeOH), mp = 122-124 °C. ¹H NMR (400 MHz, Methanol-*d*₄) δ 4.38 (1H, dd, $J = 11.0, 2.9$ Hz), 4.25 – 4.27 (1H, m), 4.17 (2H, dd, $J = 14.1$ Hz), 3.92 (1H, t, $J = 3.0$ Hz), 3.24 – 3.28 (1H, m), 2.30 – 2.38 (1H, m), 1.88 – 2.02 (3H, m); ¹³C NMR (100 MHz, Methanol-*d*₄) δ 170.0, 72.7, 60.0, 51.4, 50.9, 43.4, 26.8, 25.1; IR (film) ν 3335, 2931, 1715, 1263, 820 cm⁻¹; HRMS (DART): m/z calcd for C₈H₁₅Cl₂N₂O₂ [M + H]⁺: 241.0510, found 241.0512.



***N*-((1*R**,2*R**,3*R**,6*S**)-6-Amino-3-chloro-2-hydroxycyclohexyl)-2,2-dichloroacetamide (15):** White solid (9 mg, 16%), $R_f = 0.35$ (8:2 CH₂Cl₂/MeOH), mp = 108-110 °C. ¹H NMR (400 MHz, Methanol-*d*₄) δ 6.36 (1H, s), 4.20 – 4.22 (1H, m), 4.17 (1H, dd, $J = 10.8, 2.9$ Hz), 3.04 (1H, td, $J = 10.7, 5.2$ Hz), 2.26 – 2.35 (1H, m), 1.73 – 1.87 (3H, m); ¹³C NMR (100 MHz, Methanol-*d*₄) δ 167.0, 72.6, 67.7, 60.7, 54.7, 49.9, 27.7, 27.6; IR (film) ν 3416, 2930, 1714, 820 cm⁻¹; HRMS (DART): m/z calcd for C₈H₁₄Cl₃N₂O₂ [M + H]⁺: 275.0120, found 275.0112.

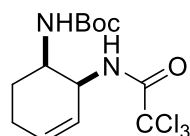


tert-Butyl((1*S,2*R**,3*R**,4*R**)-4-chloro-2-(2-chloroacetamido)-3-hydroxycyclohexyl)-carbamate (**16**):** To a solution of **14** (25 mg, 0.104 mmol) in CH₂Cl₂ (5 mL) at 0 °C was added Et₃N (29 μL, 0.208 mmol), followed by dropwise addition of di-*tert*-butyl dicarbonate (Boc₂O, 34 μL, 0.156 mmol). The reaction mixture was warmed to room temperature and was stirred for an additional 12 h. The solvent was then evaporated in vacuo, and the crude mixture was purified by silica gel column chromatography (1:1 Hexane: EtOAc) to afford compound **16** as a white solid (31 mg 88%), *R_f* = 0.50 (1:1 Hexane/EtOAc), mp = 130-133 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.31 (1H, d, *J* = 8.2 Hz), 4.78 (1H, d, *J* = 9.2 Hz), 4.27 (1H, ddd, *J* = 11.3, 8.8, 2.6 Hz), 4.21 – 4.22 (1H, m), 4.15 (1H, s), 4.01 (2H, s), 3.86 – 3.95 (1H, m), 3.44 (1H, s), 2.25 – 2.42 (1H, s), 1.87 – 1.91 (2H, m), 1.75 – 1.82 (1H, m), 1.42 (9H, s); ¹³C NMR (100 MHz, CDCl₃) δ 166.9, 156.6, 80.1, 72.4, 58.8, 52.6, 48.5, 42.6, 28.5, 27.1, 26.4; IR (film) ν 3310, 1682, 1366, 1164, 831 cm⁻¹; HRMS (DART): *m/z* calcd for C₁₃H₂₃Cl₂N₂O₄ [M + H]⁺ : 341.1034, found 341.1023.



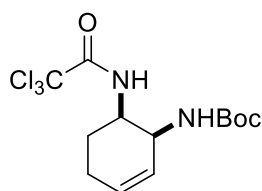
tert-Butyl((1*R,2*S**)-2-(2,2,2-trichloroacetamido)cyclohex-3-en-1-yl)carbamate (**17**):** To a solution of azide **6i** (80 mg, 0.283 mmol) in THF/water (10 mL of 4:1 v/v mixture) was added polymer-bound triphenylphosphine (113 mg of 3 mmol/g resin, 0.339 mmol) at room temperature and the resulting suspension was stirred at 65 °C for 10 h. The reaction mixture was then cooled to room temperature and filtered through a short pad of Celite and washed with CH₂Cl₂ (2 x 10 mL). The combined filtrates were concentrated under reduced pressure and the residue dissolved in CH₂Cl₂ (20 mL). The resulting solution was washed with water (10 mL) and dried over MgSO₄, filtered and concentrated under reduced pressure to give a yellow oil as mixture of isomers. The crude mixture was dissolved in CH₂Cl₂ (10 mL) and Et₃N

(79 μ L, 0.567 mmol) added, followed by dropwise addition of di-*tert*-butyl dicarbonate (Boc₂O, 92 μ L, 0.424 mmol). Then the reaction mixture was warmed to room temperature and was stirred an additional 12 h. The solvent was then evaporated in vacuo, and the crude was purified by silica gel column chromatography (2:1, Hexane: EtOAc) to afford two products **17** and **18** in 2:1 ratio.



17

***tert*-Butyl ((1*R**,2*S**)-2-(2,2,2-trichloroacetamido)cyclohex-3-en-1-yl)carbamate (17):** white solid (52 mg, 51%), R_f = 0.50 (2:1 Hexane/EtOAc), mp = 80-82 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.85 (1H, s), 5.88 – 5.92 (1H, m), 5.66 – 5.71 (1H, m), 4.58 (1H, s), 4.31 – 4.32 (1H, m), 3.96 – 3.97 (1H, m), 2.17 – 2.29 (2H, m), 2.07 – 2.13 (1H, m), 1.53 – 1.63 (1H, m), 1.43 (9H, s); ¹³C NMR (100 MHz, CDCl₃) δ 162.0, 156.5, 131.9, 124.8, 92.9, 80.8, 52.4, 47.4, 28.4, 24.5, 22.4; IR (film) ν 3310, 1682, 1366, 1164, 831 cm⁻¹; HRMS (DART): m/z calcd for C₁₃H₂₀Cl₃N₂O₃ [M + H]⁺ : 357.0539, found 357.0549.



18

***tert*-Butyl ((1*S**,6*R**)-6-(2,2,2-trichloroacetamido)cyclohex-2-en-1-yl)carbamate (18):** White solid (24 mg, 24%), R_f = 0.45 (2:1 Hexane/EtOAc), mp = 75-78 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.07 (1H, s), 5.87 – 5.92 (1H, m), 5.61 – 5.63 (1H, m), 4.74 (1H, d, J = 8.1 Hz), 4.60 – 4.61 (1H, m), 4.09 (1H, s), 2.10 – 2.26 (2H, m), 1.87 – 1.92 (1H, m), 1.72– 1.79 (1H, m), 1.43 (9H, s); ¹³C NMR (100 MHz, CDCl₃) δ 161.9, 155.9, 130.7, 125.2, 92.8, 80.3, 50.0, 47.5, 28.5, 25.2, 22.1; IR (film) ν 3310, 2981, 1664, 820 cm⁻¹; HRMS (DART): m/z calcd for C₁₃H₂₀Cl₃N₂O₃ [M + H]⁺ : 357.0539, found 357.0537.

Crystal data and structure refinement for 13

Data were collected on a Bruker Kappa APEX-DUO diffractometer using a Copper ImuS (microsource) tube with multi-layer optics and were measured using a combination of ϕ scans and ω scans. The data were processed using APEX3 (Bruker, 2018). Absorption corrections were carried out using SADABS (Krause et al., 2015). The structures were solved using SHELXT (Sheldrick, 2015) and refined using SHELXL-2018 (Sheldrick, 2015) for full-matrix least-squares refinement that was based on F^2 .

Identification code	d18149a_a	
Empirical formula	C ₈ H ₉ Cl ₃ N ₄ O ₂	
Formula weight	299.54	
Temperature	150(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	Pbca	
Unit cell dimensions	a = 13.5358(5) Å	a = 90°.
	b = 8.9392(3) Å	b = 90°.
	c = 19.6999(8) Å	g = 90°.
Volume	2383.67(15) Å ³	
Z	8	
Density (calculated)	1.669 Mg/m ³	
Absorption coefficient	6.962 mm ⁻¹	
F(000)	1216	
Crystal size	0.250 x 0.040 x 0.030 mm ³	
Theta range for data collection	4.489 to 67.239°.	
Index ranges	-15 ≤ h ≤ 16, -10 ≤ k ≤ 10, -23 ≤ l ≤ 23	
Reflections collected	42953	
Independent reflections	2124 [R(int) = 0.0458]	
Completeness to theta = 67.239°	99.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7529 and 0.4914	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	2124 / 0 / 158	
Goodness-of-fit on F ²	1.025	
Final R indices [I > 2σ(I)]	R1 = 0.0238, wR2 = 0.0597	
R indices (all data)	R1 = 0.0253, wR2 = 0.0609	
Extinction coefficient	n/a	

Largest diff. peak and hole

0.225 and -0.220 e.Å⁻³

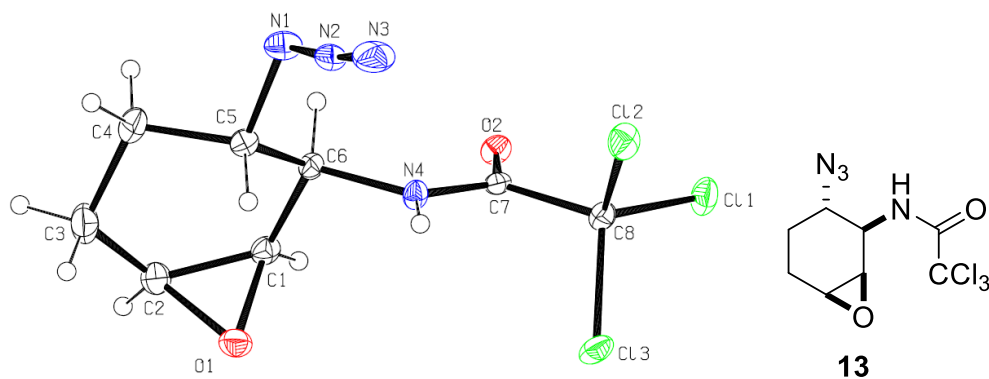


Figure 1. ORTEP of Compound **13**

Crystallographic data for compound **13** deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 1878600.

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- 6) (a) Overman, L. E. *J. Am. Chem. Soc.* **1974**, *96*, 597-599. (b) Overman, L. E. *Org. Synth.* **1978**, *58*, 4-11.

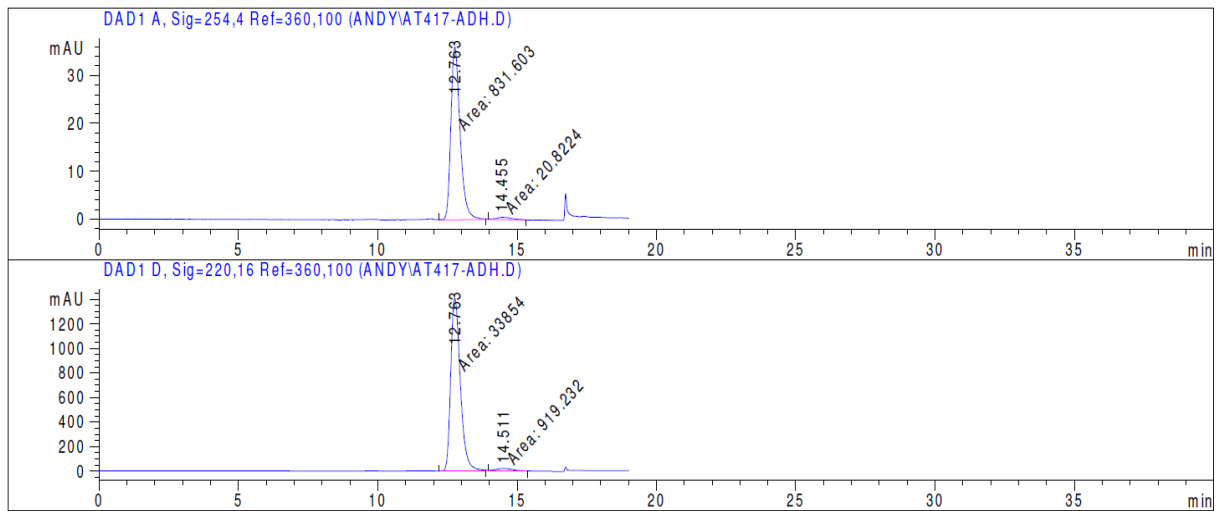
Chiral HPLC Chromatogram of (+)-3a

Data File C:\Chem32\1\DATA\ANDY\AT417-ADH.D
 Sample Name: AT417ADH

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Acq. Operator   : Andy
Acq. Instrument : Instrument 1
Injection Date  : 9/13/2010 2:29:32 AM
Location        : Vial 4
Inj Volume     : 4 µl

Acq. Method    : C:\CHEM32\1\METHODS\FARHAD.M
Last changed   : 9/13/2010 2:28:46 AM by Andy
                (modified after loading)
Analysis Method: C:\CHEM32\1\METHODS\FARHAD.M
Last changed   : 9/13/2010 2:49:17 AM by Andy
                (modified after loading)
Sample Info    :
  
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Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.763	MM	0.3845	831.60260	36.04412	97.5573
2	14.455	MM	0.6936	20.82245	5.00367e-1	2.4427

Totals : 852.42505 36.54448

Signal 2: DAD1 D, Sig=220,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.763	MM	0.4006	3.38540e4	1408.41138	97.3565
2	14.511	MM	0.7111	919.23163	21.54418	2.6435

Totals : 3.47733e4 1429.95556

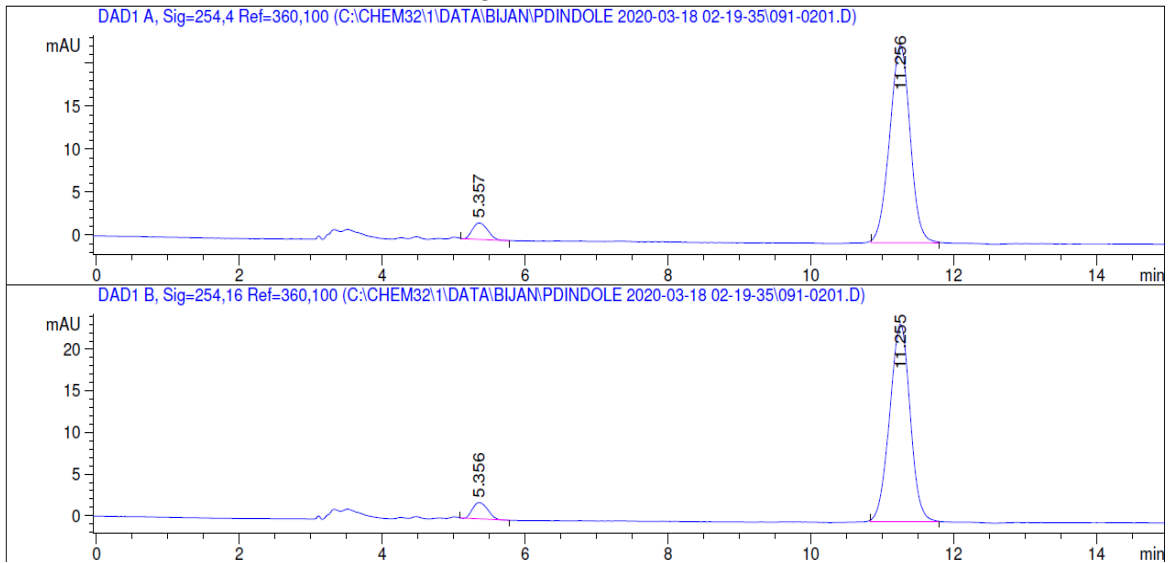
Chiral HPLC Chromatogram of (+)-6a

Data File C:\CHEM32\1\DATA\BIJAN\PDINDOLE 2020-03-18 02-19-35\091-0201.D
 Sample Name: KLH-D-33

```

=====
Acq. Operator   : AW                               Seq. Line :    2
Acq. Instrument : HPLC_2                           Location  : Vial 91
Injection Date  : 3/18/2020 2:36:27 AM             Inj       :    1
                                                    Inj Volume: 5 µl

Acq. Method     : C:\Chem32\1\DATA\BIJAN\PDINDOLE 2020-03-18 02-19-35\BM.M
Last changed    : 3/18/2020 2:19:32 AM by AW
Analysis Method : C:\CHEM32\1\DATA\BIJAN\PDINDOLE 2020-03-18 02-19-35\BM.M
Last changed    : 3/18/2020 11:24:17 AM by AW
                (modified after loading)
  
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Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.357	BB	0.2355	27.61417	1.87901	5.6879
2	11.256	BB	0.3131	457.87256	22.91665	94.3121

Totals : 485.48673 24.79565

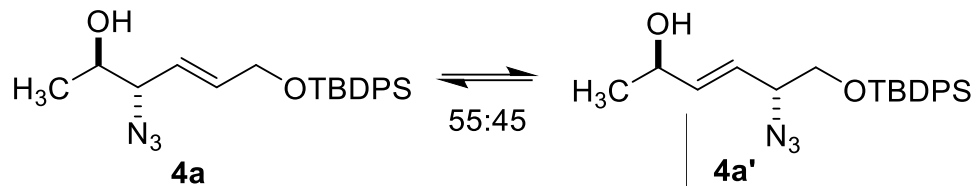
Signal 2: DAD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.356	BB	0.2341	28.39489	1.94752	5.6444
2	11.255	BB	0.3132	474.66849	23.74674	94.3556

Totals : 503.06338 25.69426

Selected ^1H -NMR and ^{13}C -NMR Spectra

^1H NMR of Compound 4a / 4a' (CDCl_3 ; 400 Hz)



Sample: AT056_B

Sample ID: s_20080827_73

File: timothy/students/atjeng/vnmrsys/data/20080827-AT056_B_PROTON-002.fid

Pulse Sequence: s2pul

Solvent: cdc13

Temp. 25.0 C / 298.1 K

Sample #74, Operator: atjeng

File: 20080827-AT056_B_PROTON-002

VNMRS-400 "pekkle.nmr"

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 2.992 sec

Width 6398.0 Hz

16 repetitions

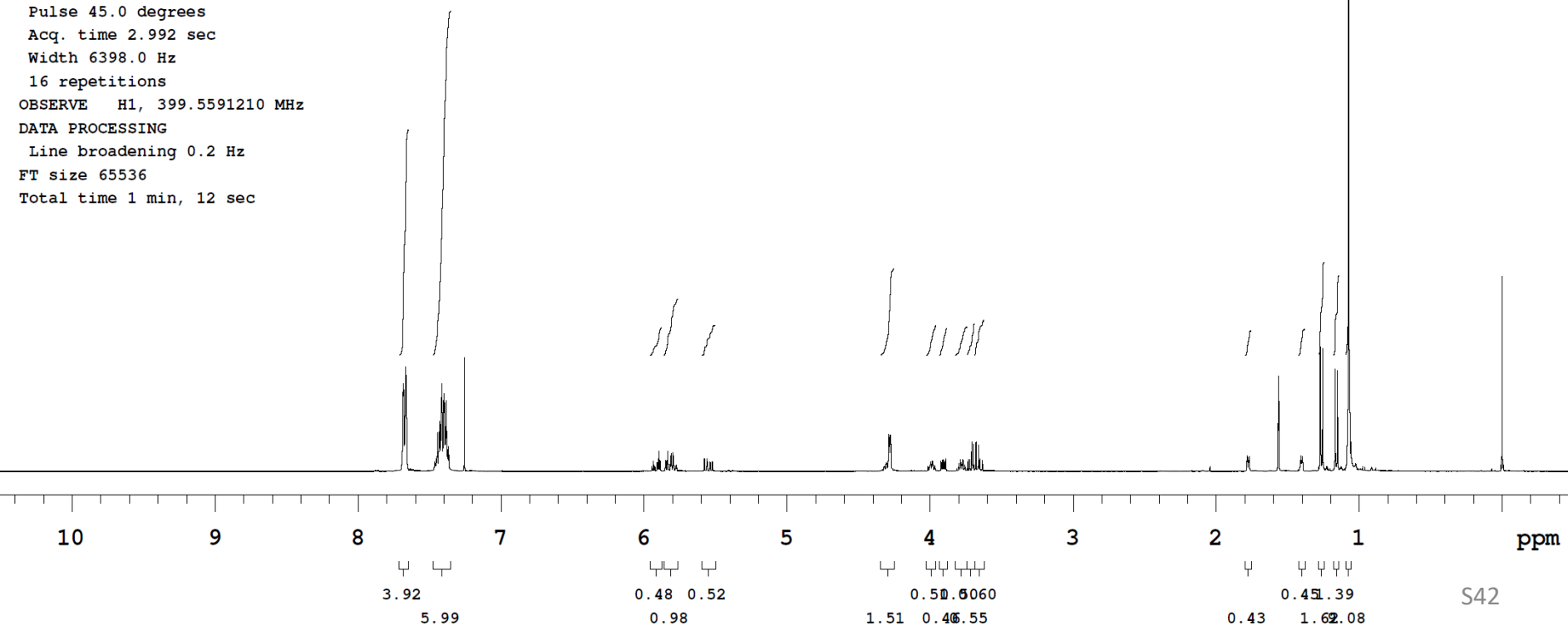
OBSERVE H1, 399.5591210 MHz

DATA PROCESSING

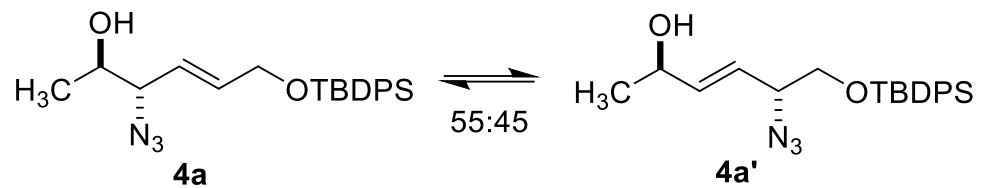
Line broadening 0.2 Hz

FT size 65536

Total time 1 min, 12 sec



^{13}C NMR of Compound 4a / 4a' (CDCl_3 ; 100 MHz)

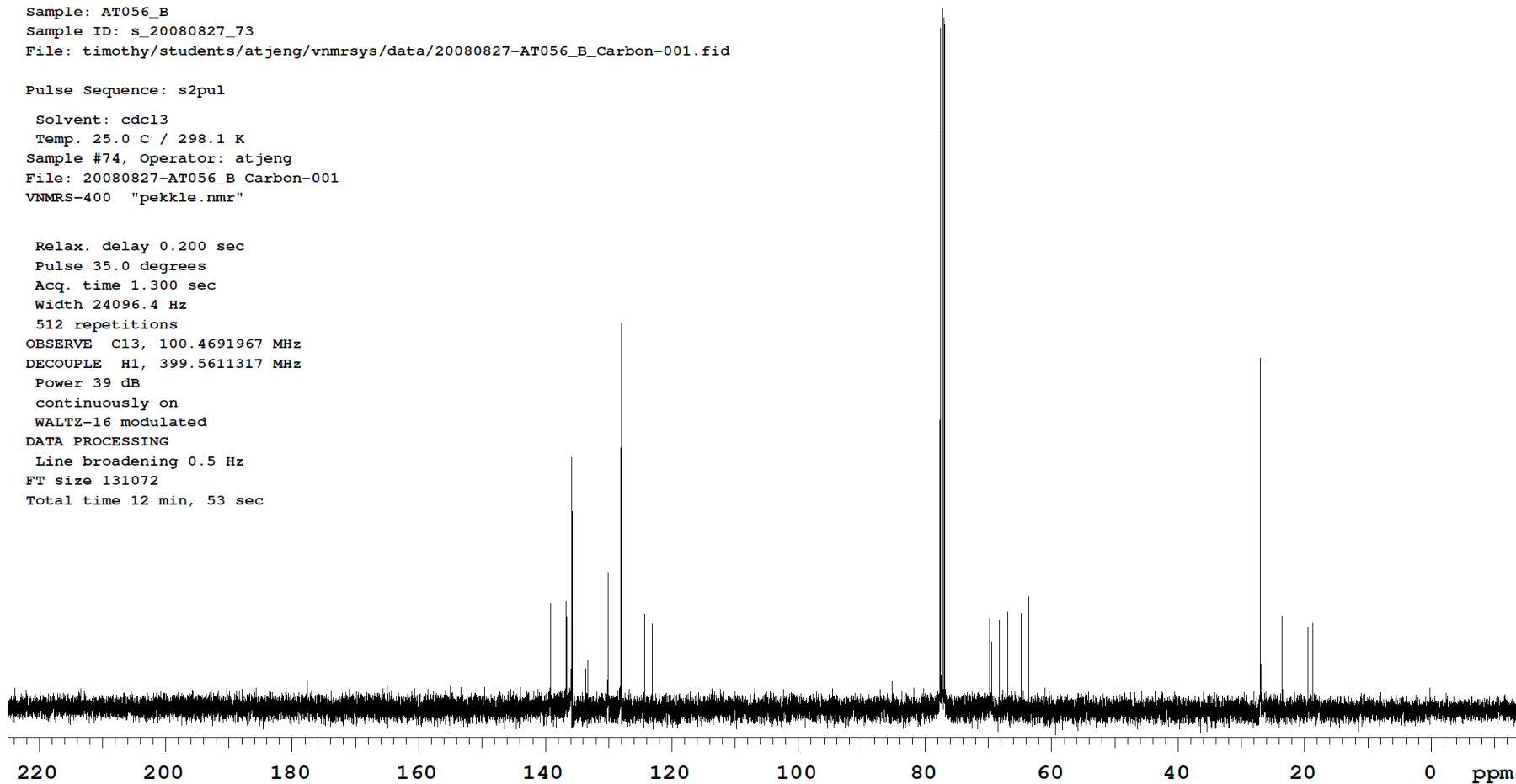


Sample: AT056_B
Sample ID: s_20080827_73
File: timothy/students/atjeng/vnmrsys/data/20080827-AT056_B_Carbon-001.fid

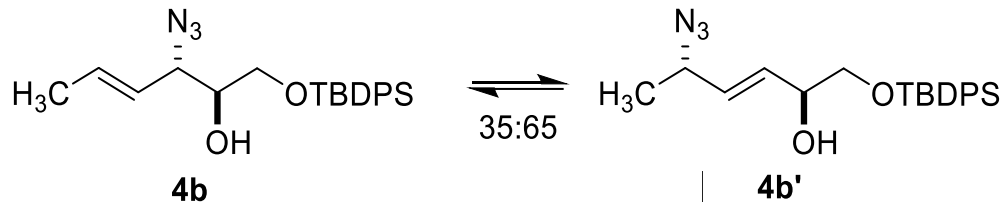
Pulse Sequence: s2pul

Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Sample #74, Operator: atjeng
File: 20080827-AT056_B_Carbon-001
VNMR-400 "pekkle.nmr"

Relax. delay 0.200 sec
Pulse 35.0 degrees
Acq. time 1.300 sec
Width 24096.4 Hz
512 repetitions
OBSERVE C13, 100.4691967 MHz
DECOUPLE H1, 399.5611317 MHz
Power 39 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 12 min, 53 sec



^1H NMR of Compound 4b / 4b' (CDCl_3 ; 400 MHz)

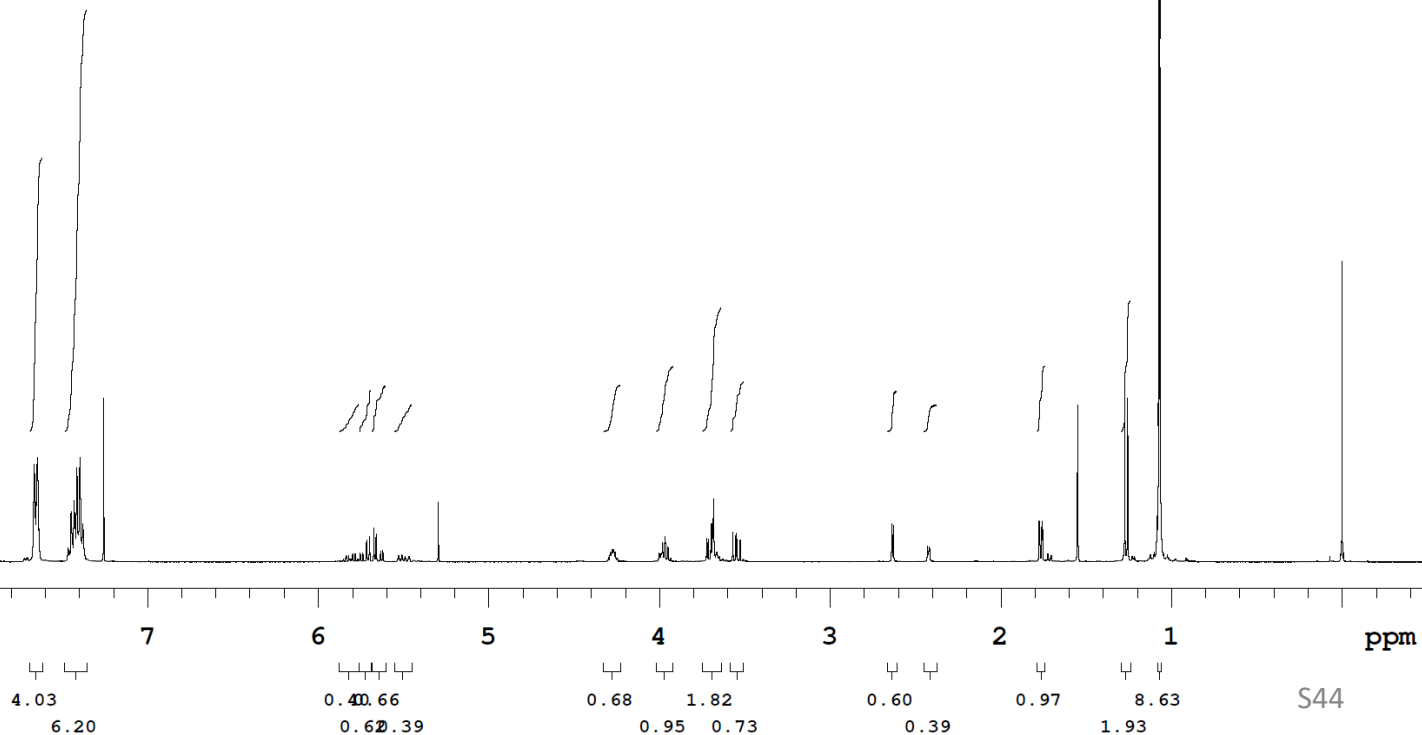


Sample: AT057_B
Sample ID: s_20080825_84
File: timothy/students/atjeng/vnmrsys/data/20080826-AT057_B_PROTON-002.fid

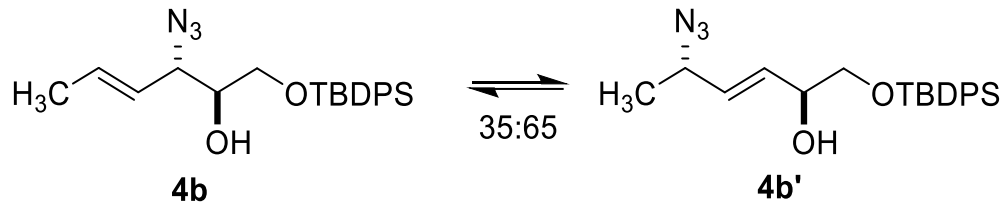
Pulse Sequence: s2pul

Solvent: cdcl_3
Temp. 25.0 C / 298.1 K
Sample #80, Operator: atjeng
File: 20080826-AT057_B_PROTON-002
VNMR-400 "pekkle.nmr"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.992 sec
Width 6398.0 Hz
16 repetitions
OBSERVE H1, 399.5591208 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 12 sec



^{13}C NMR of Compound 4b / 4b' (CDCl_3 ; 100 MHz)

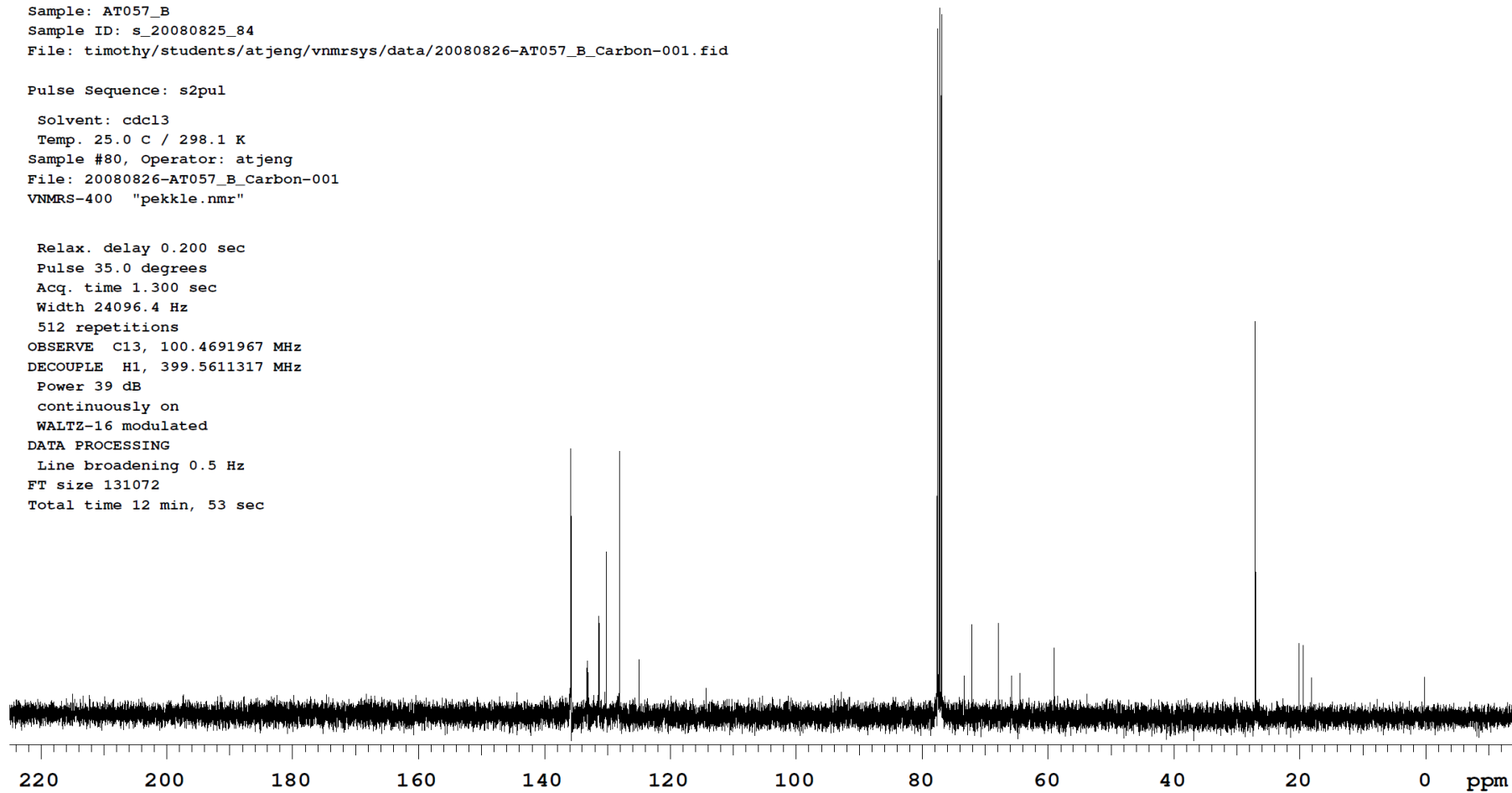


Sample: AT057_B
Sample ID: s_20080825_84
File: timothy/students/atjeng/vnmrsys/data/20080826-AT057_B_Carbon-001.fid

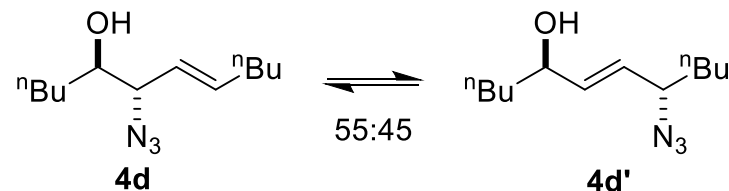
Pulse Sequence: s2pul

Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Sample #80, Operator: atjeng
File: 20080826-AT057_B_Carbon-001
VNMR-400 "pekkle.nmr"

Relax. delay 0.200 sec
Pulse 35.0 degrees
Acq. time 1.300 sec
Width 24096.4 Hz
512 repetitions
OBSERVE C13, 100.4691967 MHz
DECOUPLE H1, 399.5611317 MHz
Power 39 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 12 min, 53 sec



^1H NMR of Compound 4d / 4d' (CDCl_3 ; 400 MHz)

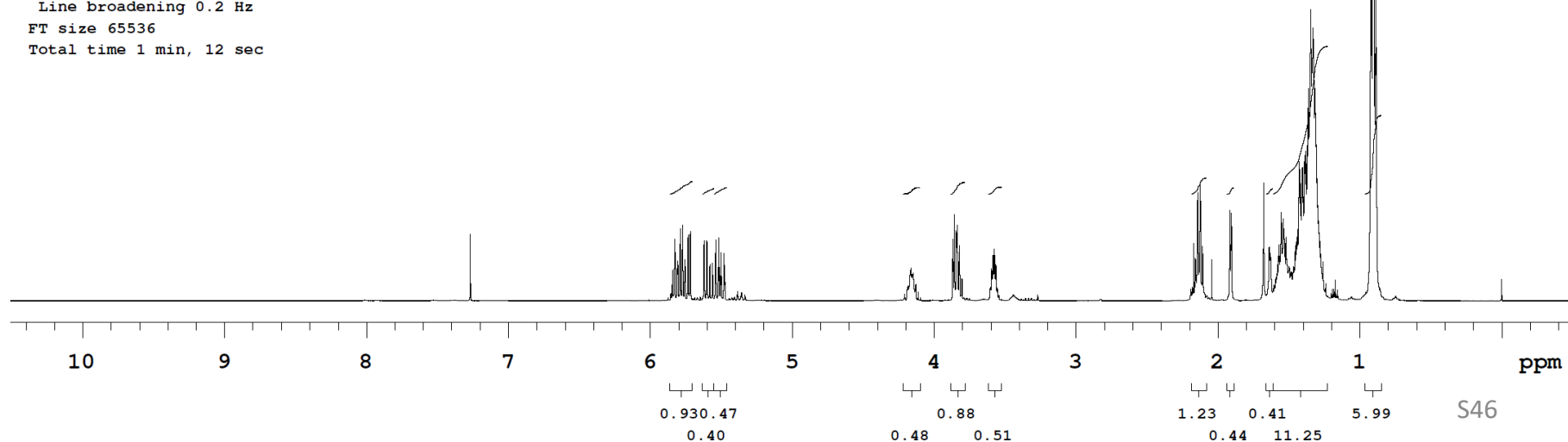


Sample: AT2_196_1
Sample ID: s_20090721_01
File: timothy/students/atjeng/vnmrsys/data/20090721-AT2_196_1_PROTON-002.fid

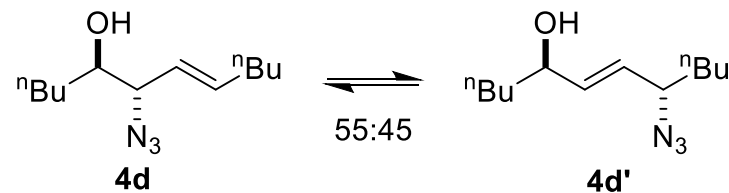
Pulse Sequence: s2pul

Solvent: cdcl_3
Temp. 25.0 C / 298.1 K
Sample #73, Operator: atjeng
File: 20090721-AT2_196_1_PROTON-002
VNMRS-400 "pekkle.nmr"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.992 sec
Width 6398.0 Hz
16 repetitions
OBSERVE H1, 399.5350131 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 12 sec



^{13}C NMR of Compound 4d / 4d' (CDCl_3 ; 75 MHz)

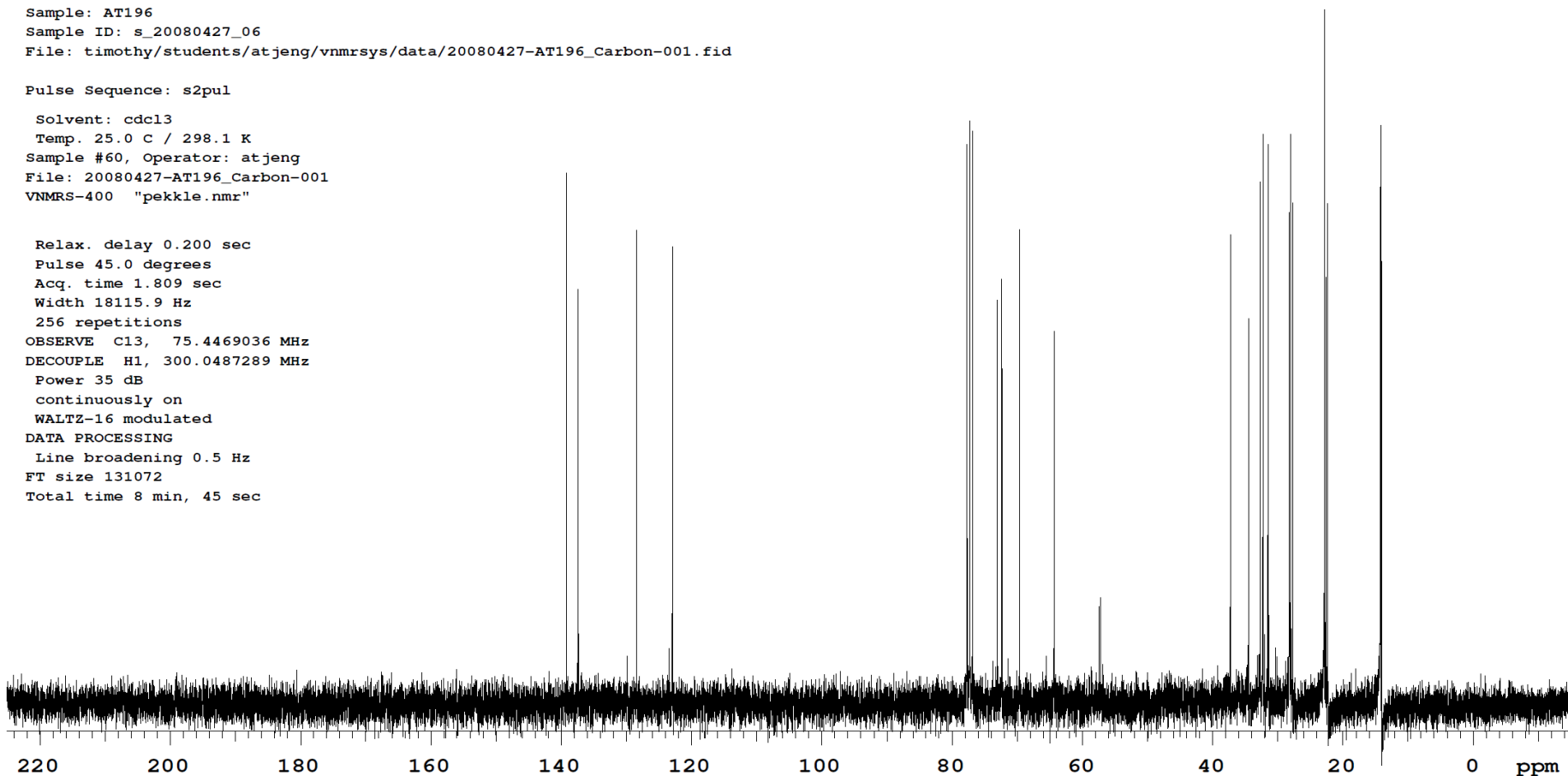


Sample: AT196
Sample ID: s_20080427_06
File: timothy/students/atjeng/vnmrsys/data/20080427-AT196_Carbon-001.fid

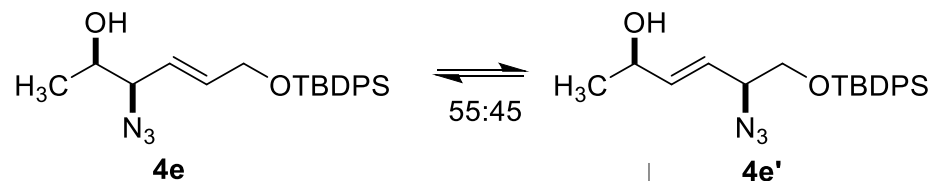
Pulse Sequence: s2pul

Solvent: cdc13
Temp. 25.0 C / 298.1 K
Sample #60, Operator: atjeng
File: 20080427-AT196_Carbon-001
VNMR-400 "pekkle.nmr"

Relax. delay 0.200 sec
Pulse 45.0 degrees
Acq. time 1.809 sec
Width 18115.9 Hz
256 repetitions
OBSERVE C13, 75.4469036 MHz
DECOUPLE H1, 300.0487289 MHz
Power 35 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 8 min, 45 sec



^1H NMR of Compound 4e / 4e' (CDCl_3 ; 300 MHz)

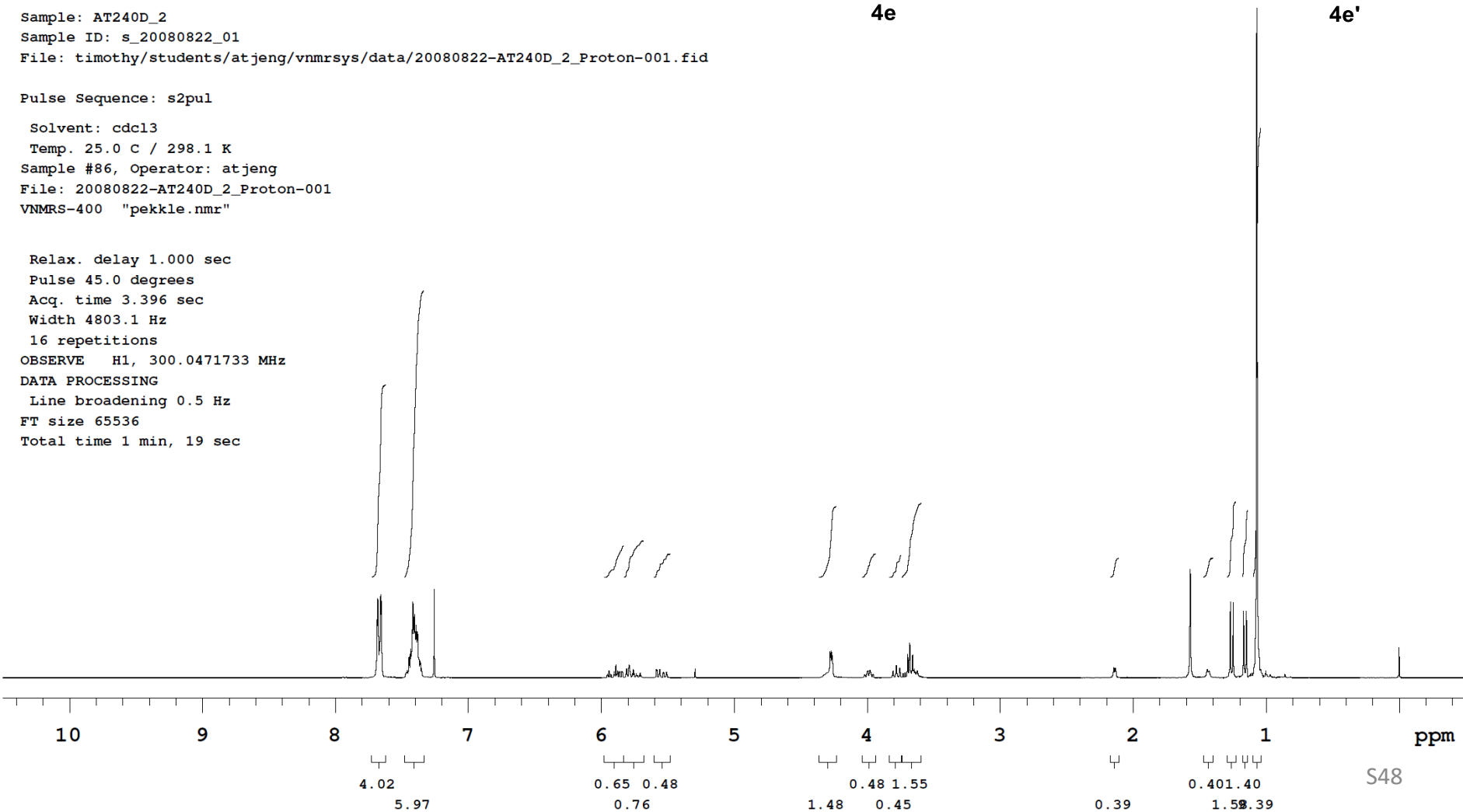


Sample: AT240D_2
Sample ID: s_20080822_01
File: timothy/students/atjeng/vnmrsys/data/20080822-AT240D_2_Proton-001.fid

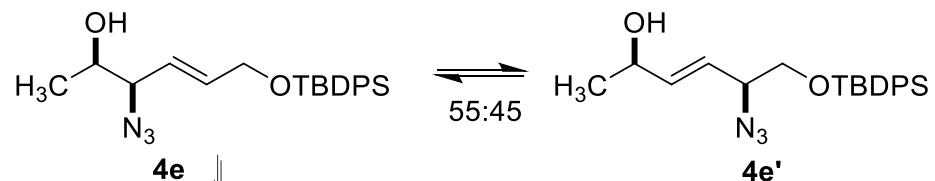
Pulse Sequence: s2pul

Solvent: cdc13
Temp. 25.0 C / 298.1 K
Sample #86, Operator: atjeng
File: 20080822-AT240D_2_Proton-001
VNMR-400 "pekkle.nmr"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 3.396 sec
Width 4803.1 Hz
16 repetitions
OBSERVE H1, 300.0471733 MHz
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 1 min, 19 sec



¹³C NMR of Compound 4e / 4e' (CDCl₃; 75 MHz)

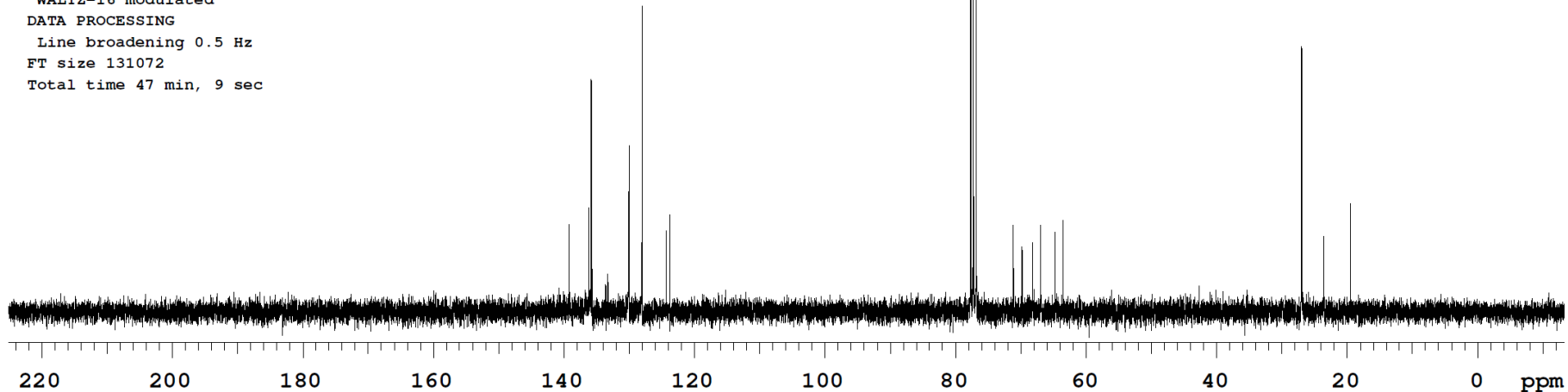


Sample: AT240D_2
Sample ID: s_20080822_01
File: timothy/students/atjeng/vnmrsys/data/20080822-AT240D_2_Carbon-001.fid

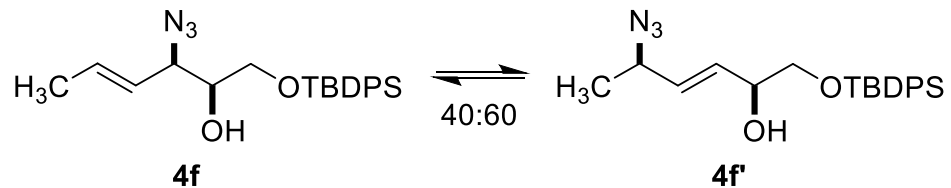
Pulse Sequence: s2pul

Solvent: cdcl3
Temp. 25.0 c / 298.1 K
Sample #86, Operator: atjeng
File: 20080822-AT240D_2_Carbon-001
VNMRS-400 "pekkle.nmr"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.809 sec
Width 18115.9 Hz
1000 repetitions
OBSERVE C13, 75.4469036 MHz
DECOUPLE H1, 300.0487289 MHz
Power 35 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 47 min, 9 sec



^1H NMR of Compound 4f / 4f' (CDCl_3 ; 300 MHz)

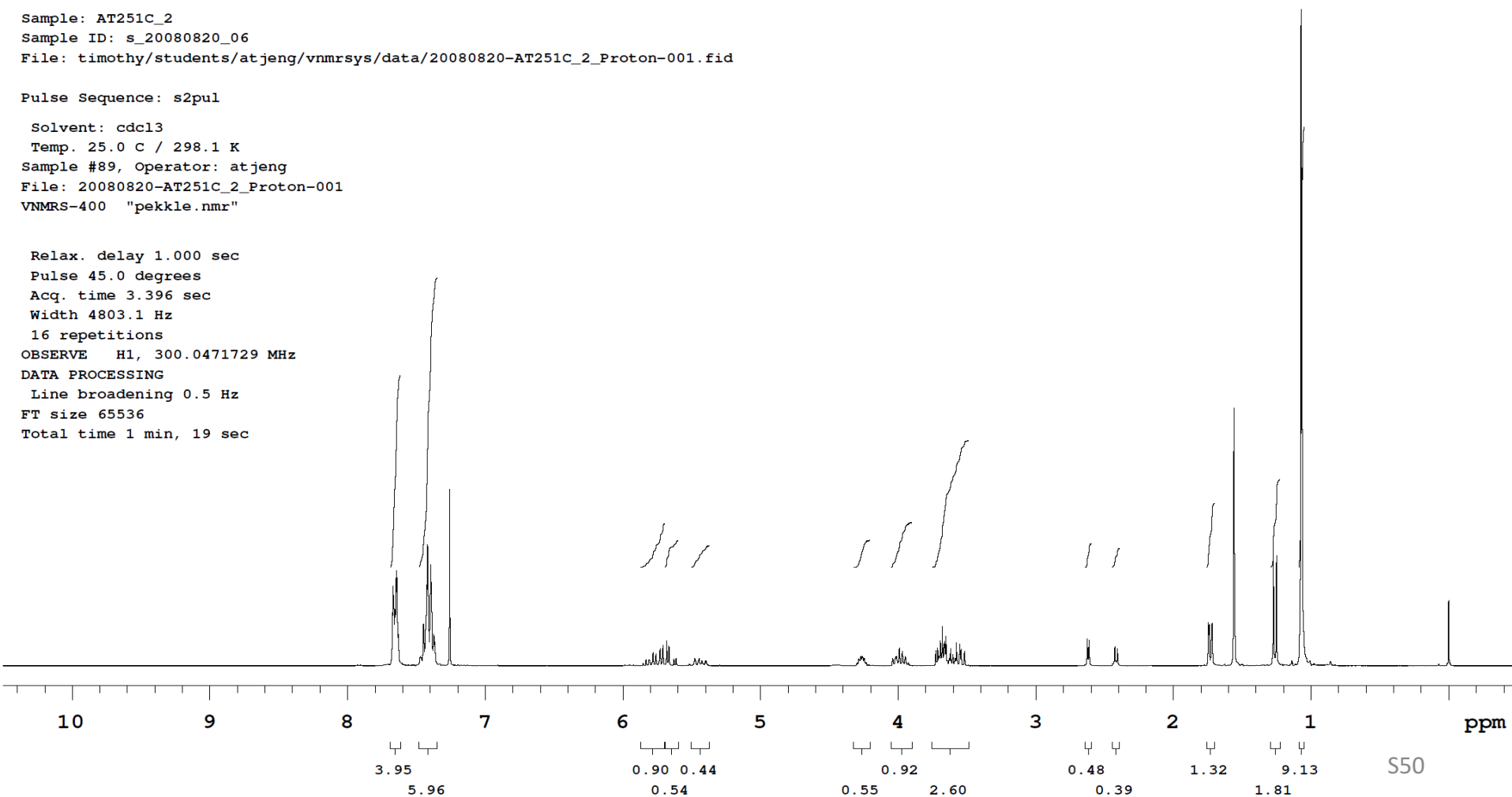


Sample: AT251C_2
Sample ID: s_20080820_06
File: timothy/students/atjeng/vnmrsys/data/20080820-AT251C_2_Proton-001.fid

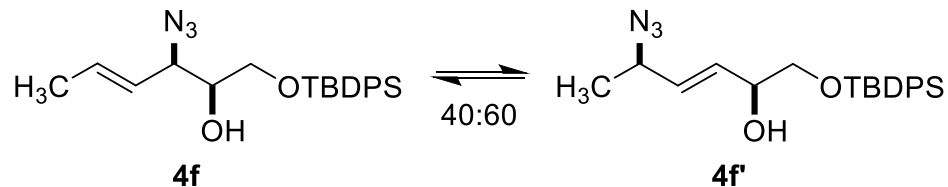
Pulse Sequence: s2pul

Solvent: cdc13
Temp. 25.0 C / 298.1 K
Sample #89, Operator: atjeng
File: 20080820-AT251C_2_Proton-001
VNMR-400 "pekkle.nmr"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 3.396 sec
Width 4803.1 Hz
16 repetitions
OBSERVE H1, 300.0471729 MHz
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 1 min, 19 sec



^{13}C NMR of Compound 4f / 4f' (CDCl_3 ; 75 MHz)

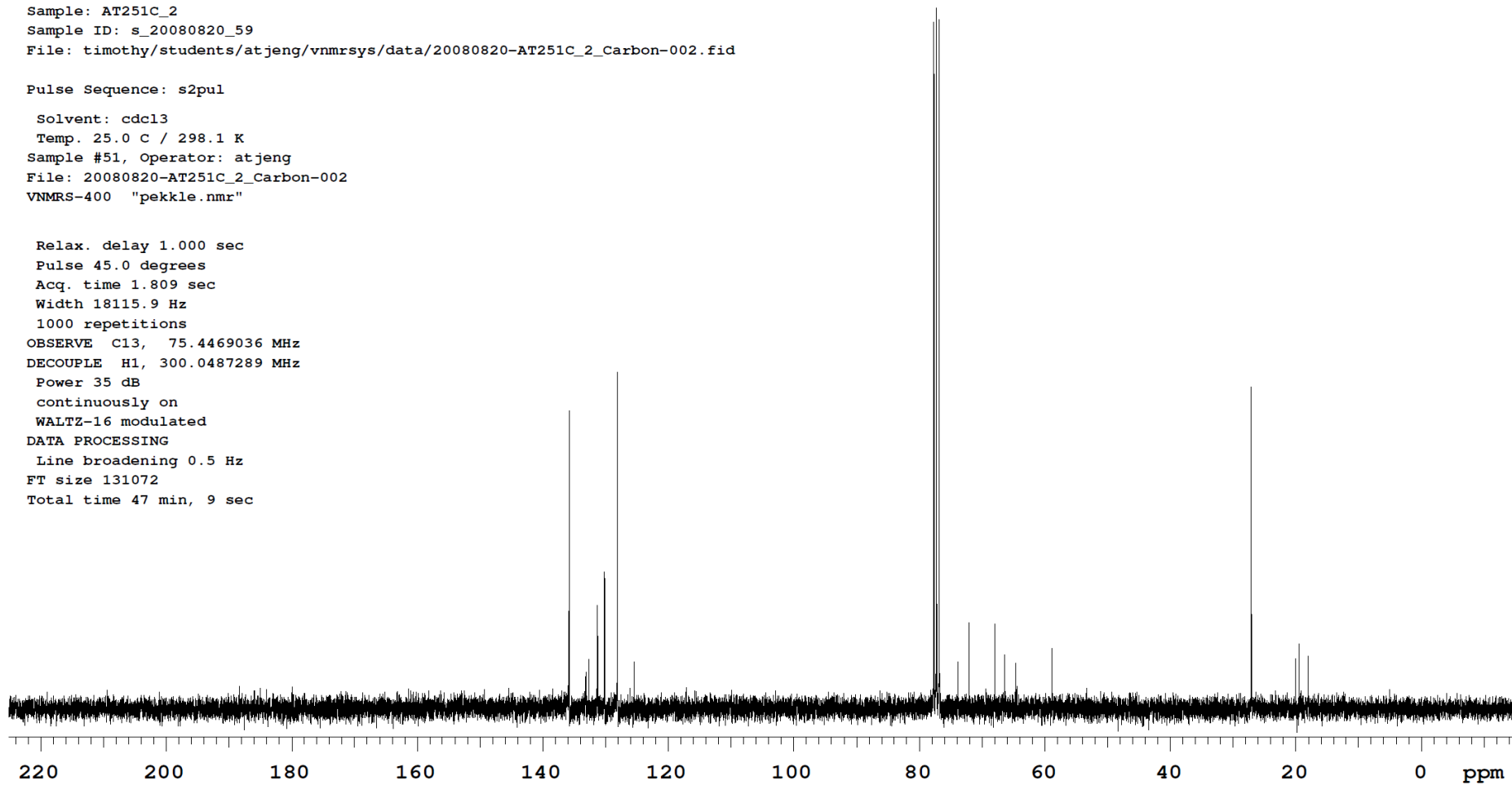


Sample: AT251C_2
Sample ID: s_20080820_59
File: timothy/students/atjeng/vnmrsys/data/20080820-AT251C_2_Carbon-002.fid

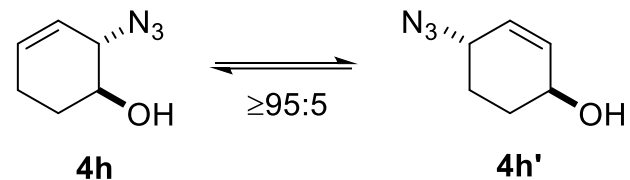
Pulse Sequence: s2pul

Solvent: cdc13
Temp. 25.0 C / 298.1 K
Sample #51, Operator: atjeng
File: 20080820-AT251C_2_Carbon-002
VNMR-400 "pekkle.nmr"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.809 sec
Width 18115.9 Hz
1000 repetitions
OBSERVE C13, 75.4469036 MHz
DECOUPLE H1, 300.0487289 MHz
Power 35 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 47 min, 9 sec



^1H NMR of Compound 4h / 4h' (CDCl_3 ; 400 MHz)

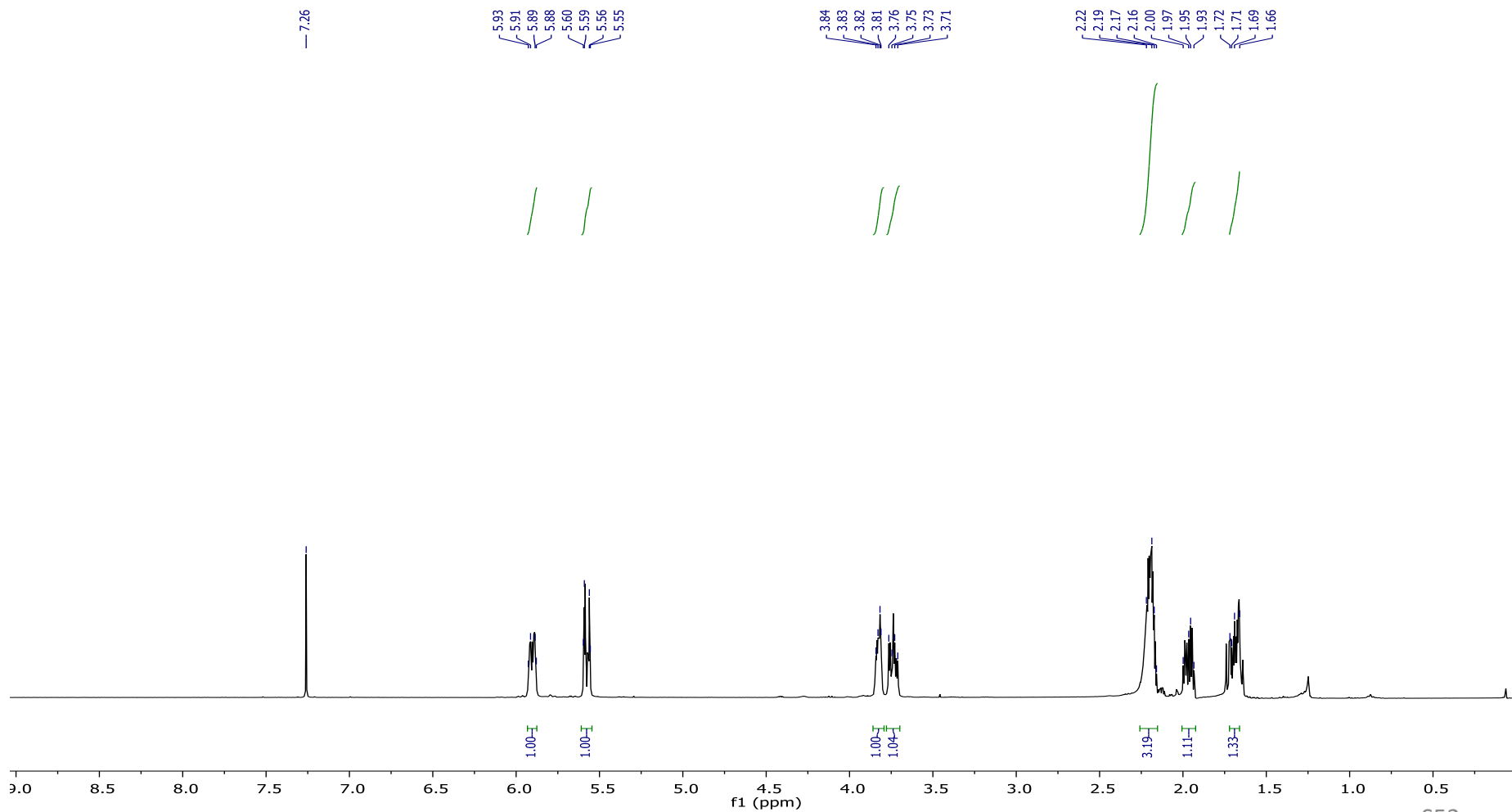


7.26

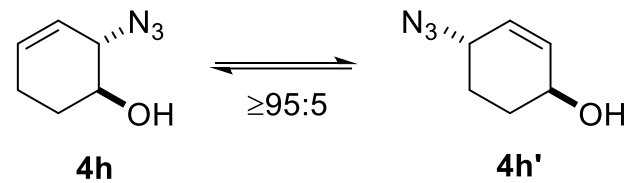
5.93
5.91
5.89
5.88
5.60
5.59
5.56
5.55

3.84
3.83
3.82
3.81
3.76
3.75
3.73
3.71

2.22
2.19
2.17
2.16
2.00
1.97
1.95
1.93
1.72
1.71
1.69
1.66



^{13}C NMR of Compound 4h / 4h' (CDCl_3 ; 100 MHz)



131.65

123.24

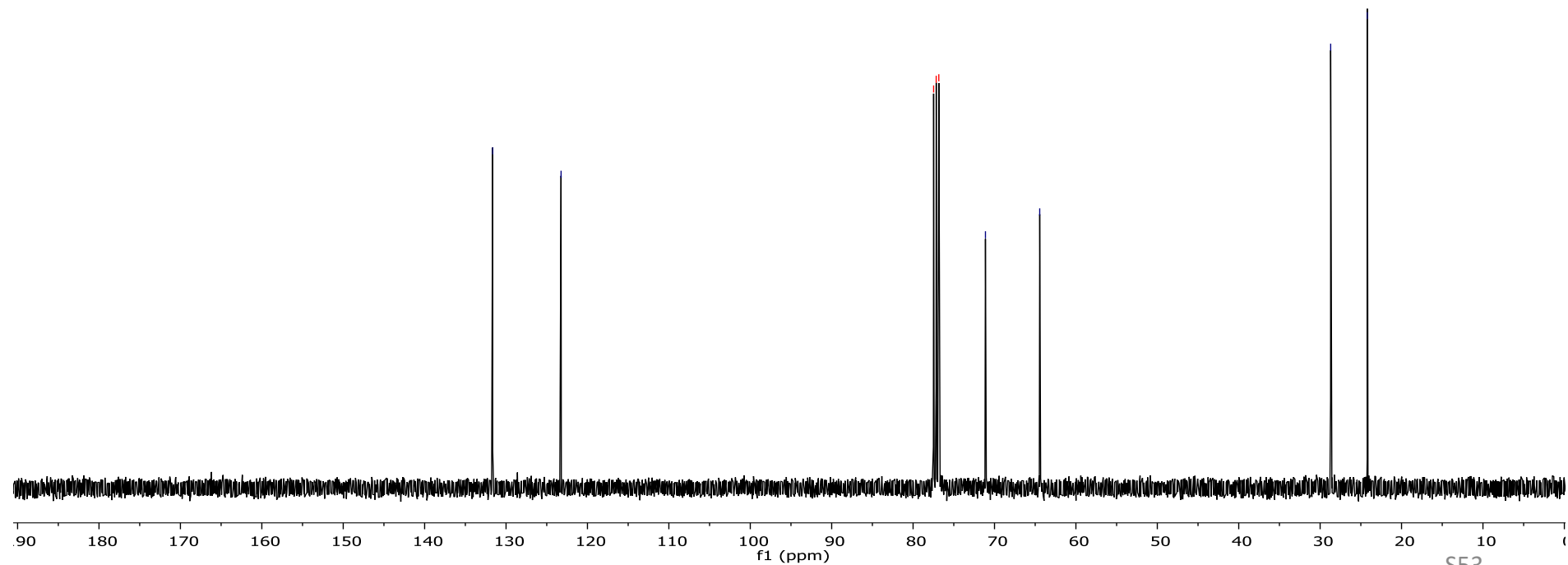
77.48 cdd3
77.16 cdd3
76.84 cdd3

71.11

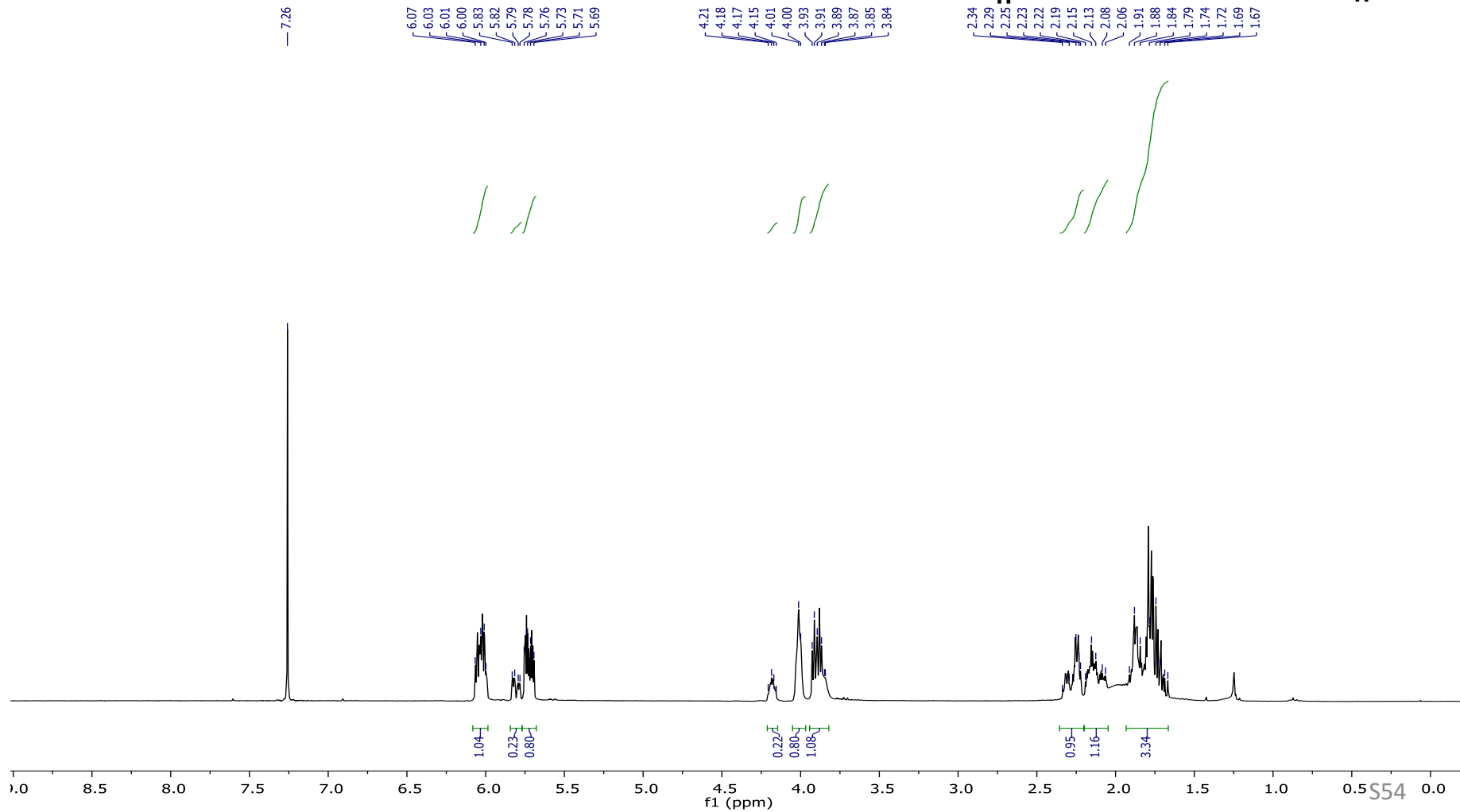
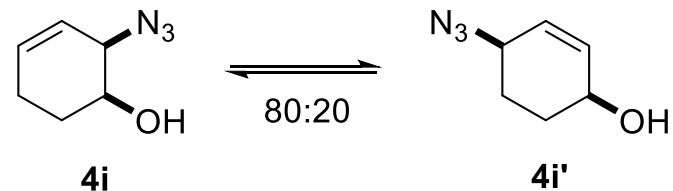
64.45

28.70

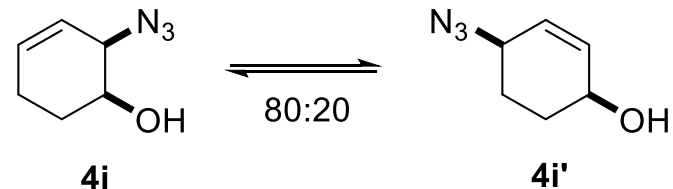
24.20



¹H NMR of Compound 4i / 4i' (CDCl₃; 400 MHz)



^{13}C NMR of Compound 4i / 4i' (CDCl_3 ; 100 MHz)

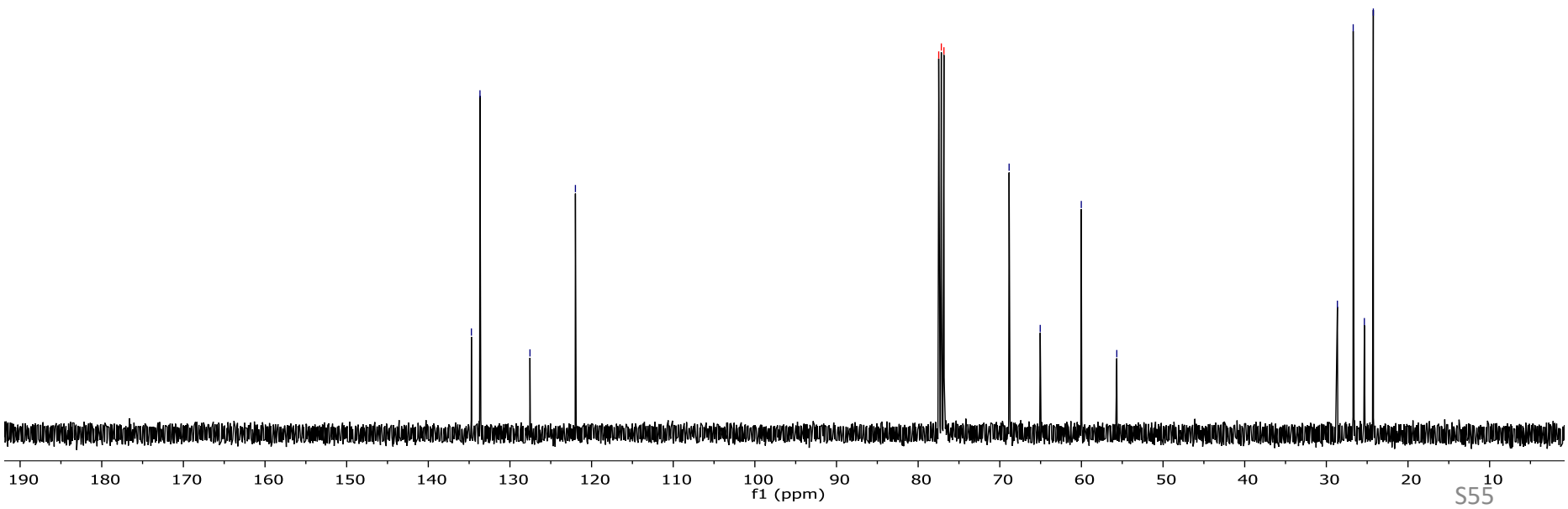


134.72
133.67
127.55
121.98

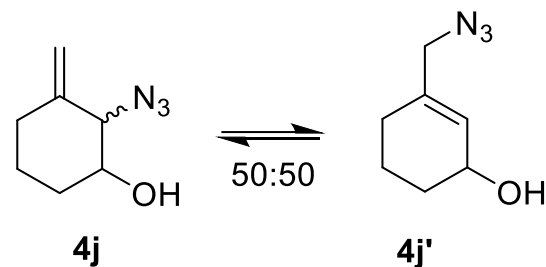
77.48 cdd3
77.16 cdd3
76.84 cdd3

68.86
65.05
60.02
55.67

28.65
26.71
25.34
24.25



^1H NMR of Compound 4j / 4j' (CDCl_3 ; 400 MHz)

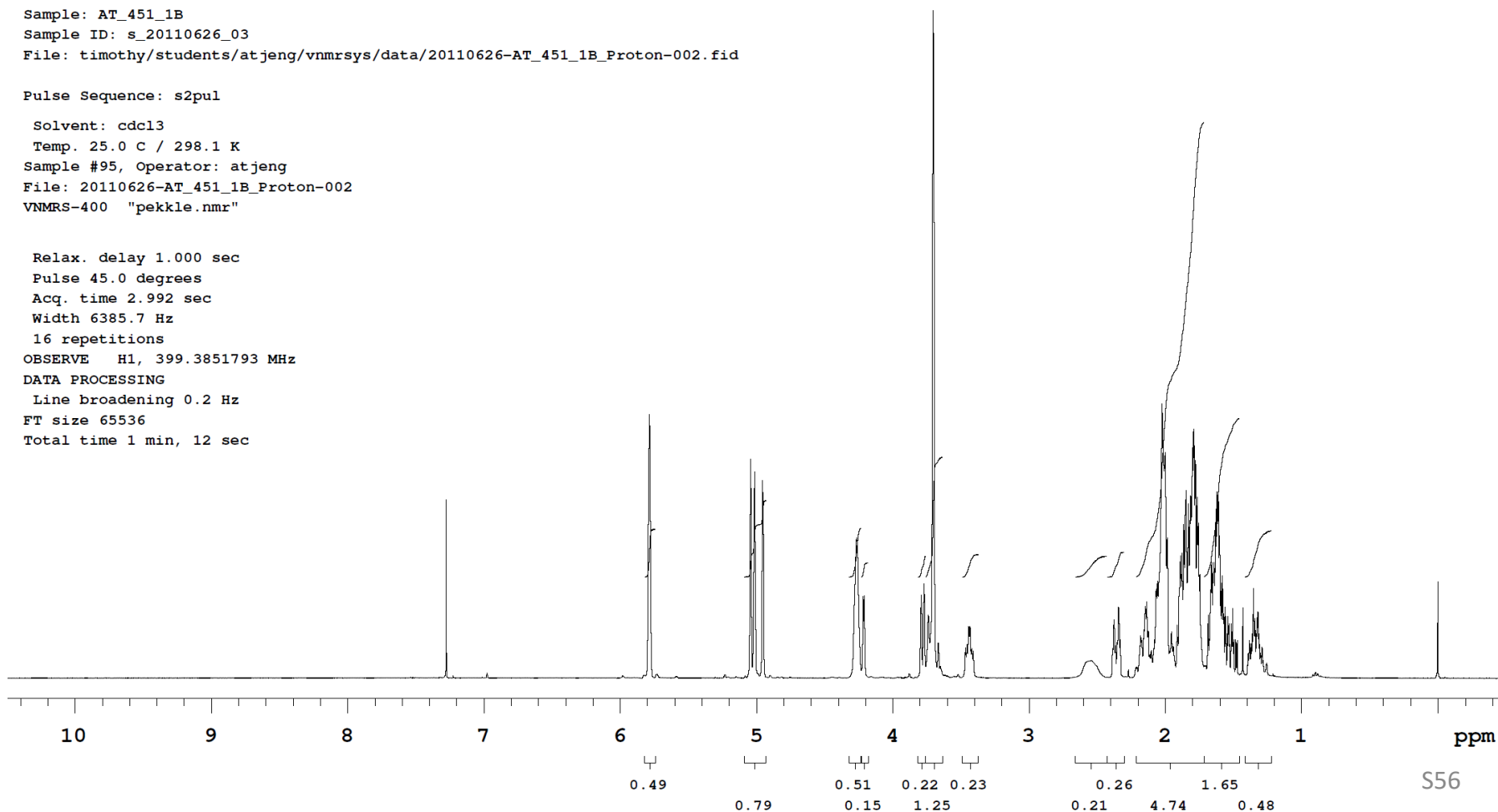


Sample: AT_451_1B
Sample ID: s_20110626_03
File: timothy/students/atjeng/vnmrsys/data/20110626-AT_451_1B_Proton-002.fid

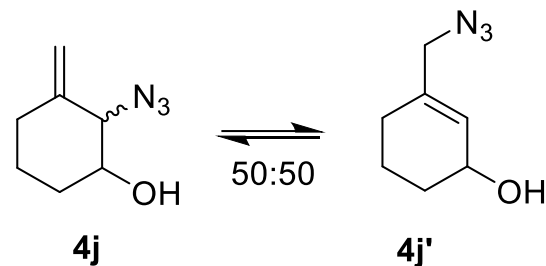
Pulse Sequence: s2pul

Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Sample #95, Operator: atjeng
File: 20110626-AT_451_1B_Proton-002
VNMR-400 "pekkle.nmr"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.992 sec
Width 6385.7 Hz
16 repetitions
OBSERVE H1, 399.3851793 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 12 sec



^{13}C NMR of Compound 4j / 4j' (CDCl₃; 100 MHz)

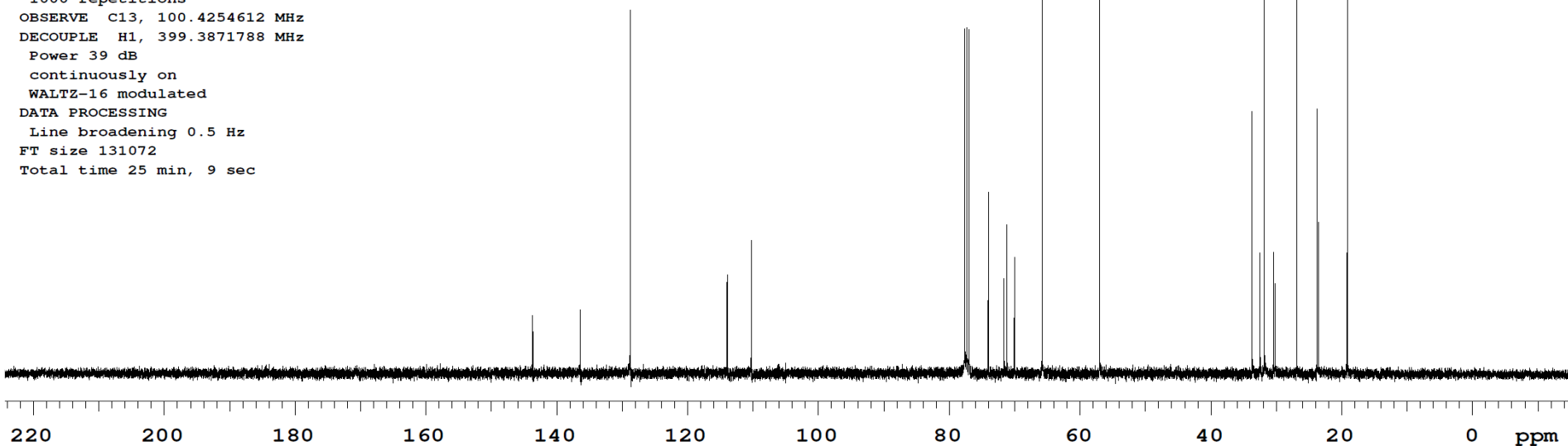


Sample: AT_451_1B
Sample ID: s_20110626_03
File: timothy/students/atjeng/vnmrsys/data/20110626-AT_451_1B_Carbon-001.fid

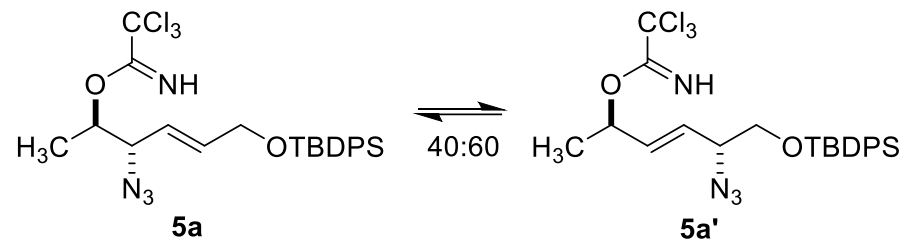
Pulse Sequence: s2pul

Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Sample #95, Operator: atjeng
File: 20110626-AT_451_1B_Carbon-001
VNMR-400 "pekkle.nmr"

Relax. delay 0.200 sec
Pulse 35.0 degrees
Acq. time 1.300 sec
Width 24096.4 Hz
1000 repetitions
OBSERVE C13, 100.4254612 MHz
DECOUPLE H1, 399.3871788 MHz
Power 39 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 25 min, 9 sec



^1H NMR of Compound 5a / 5a' (CDCl_3 ; 400 MHz)

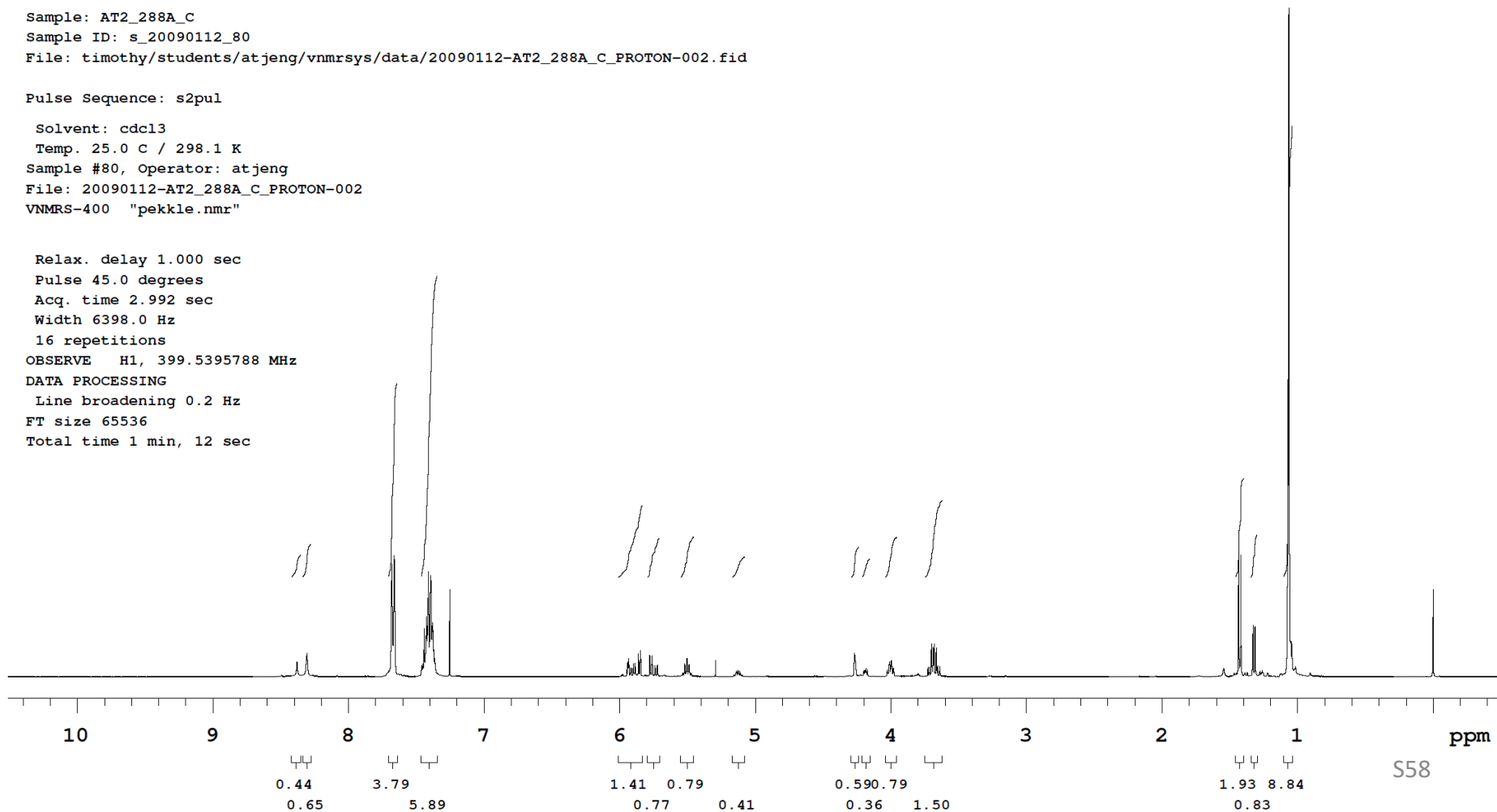


Sample: AT2_288A_C
Sample ID: s_20090112_80
File: timothy/students/atjeng/vnmrsys/data/20090112-AT2_288A_C_PROTON-002.fid

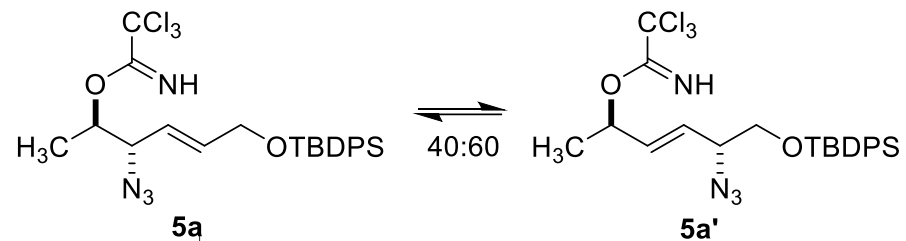
Pulse Sequence: s2pul

Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Sample #80, Operator: atjeng
File: 20090112-AT2_288A_C_PROTON-002
VNMR-400 "pekkle.nmr"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.992 sec
Width 6398.0 Hz
16 repetitions
OBSERVE H1, 399.5395788 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 12 sec



^{13}C NMR of Compound 5a / 5a' (CDCl_3 ; 100 MHz)

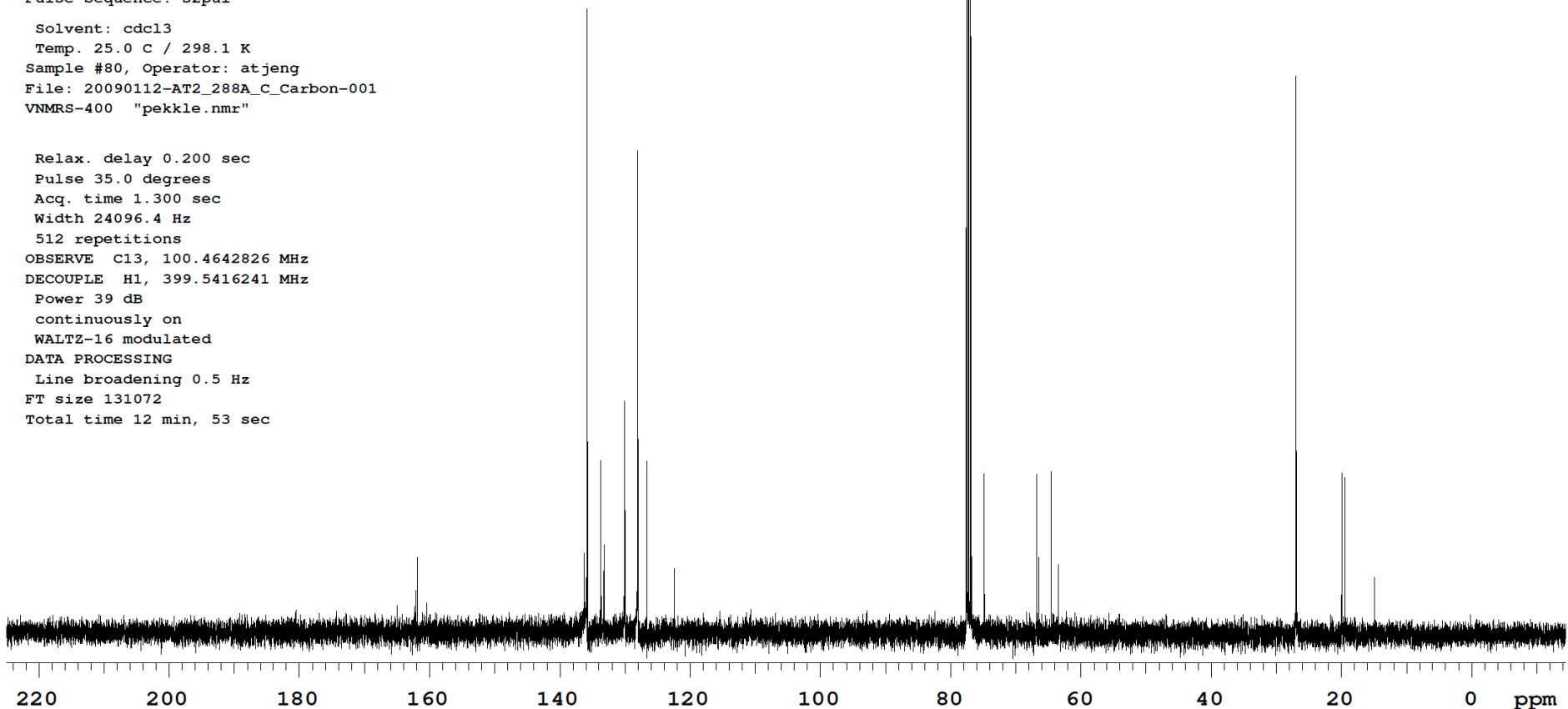


Sample: AT2_288A_C
Sample ID: s_20090112_80
File: timothy/students/atjeng/vnmrsys/data/20090112-AT2_288A_C_Carbon-001.fid

Pulse Sequence: s2pul

Solvent: cdcl3
Temp. 25.0 c / 298.1 K
Sample #80, Operator: atjeng
File: 20090112-AT2_288A_C_Carbon-001
VNMR-400 "pekkle.nmr"

Relax. delay 0.200 sec
Pulse 35.0 degrees
Acq. time 1.300 sec
Width 24096.4 Hz
512 repetitions
OBSERVE C13, 100.4642826 MHz
DECOUPLE H1, 399.5416241 MHz
Power 39 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 12 min, 53 sec



220

200

180

160

140

120

100

80

60

40

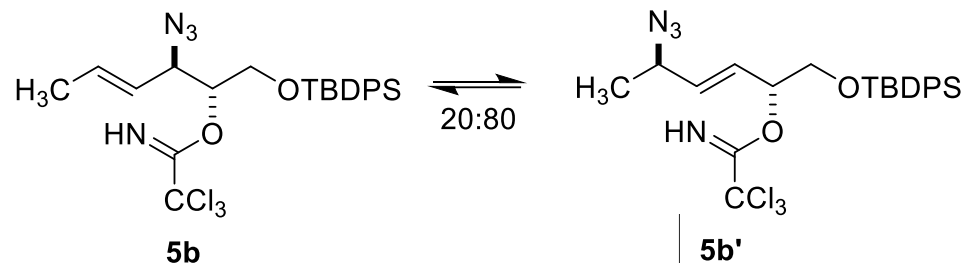
20

0

ppm

S59

^1H NMR of Compound 5b / 5b' (CDCl_3 ; 400 MHz)

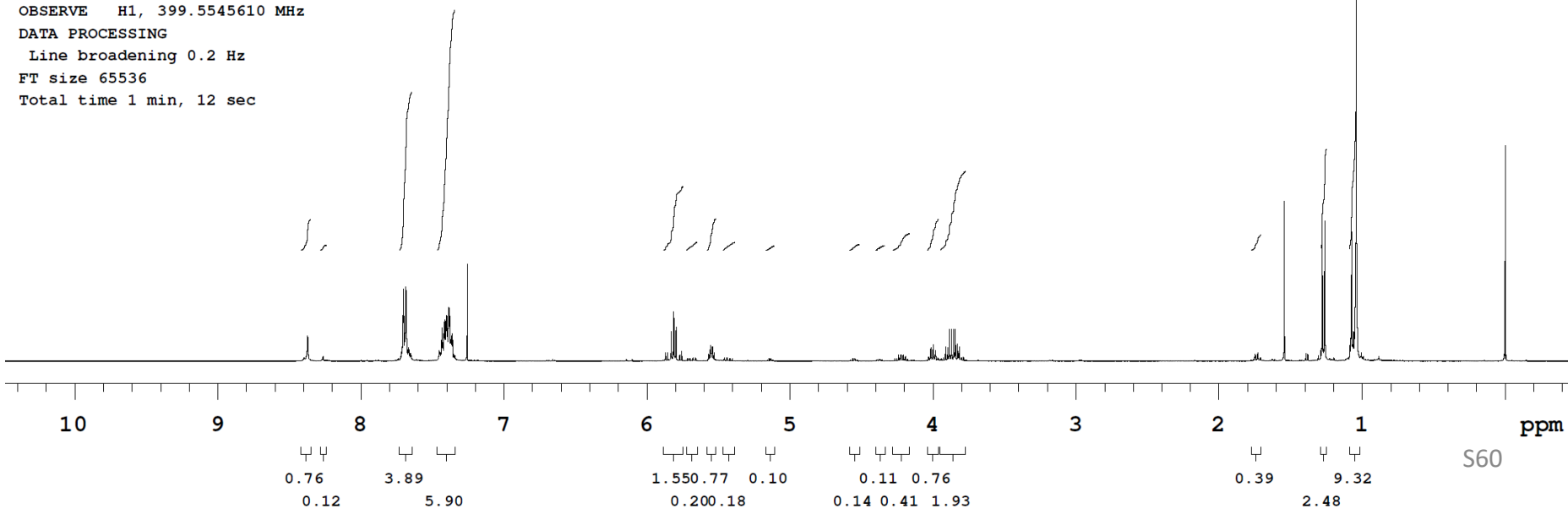


Sample: AT2_299B_2
Sample ID: s_20090514_64
File: timothy/students/atjeng/vnmrsys/data/20090514-AT2_299B_2_PROTON-002.fid

Pulse Sequence: s2pul

Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Sample #61, Operator: atjeng
File: 20090514-AT2_299B_2_PROTON-002
VNMR-400 "pekkle.nmr"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.992 sec
Width 6398.0 Hz
16 repetitions
OBSERVE H1, 399.5545610 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 12 sec



^{13}C NMR of Compound 5b / 5b' (CDCl_3 ; 75 MHz)

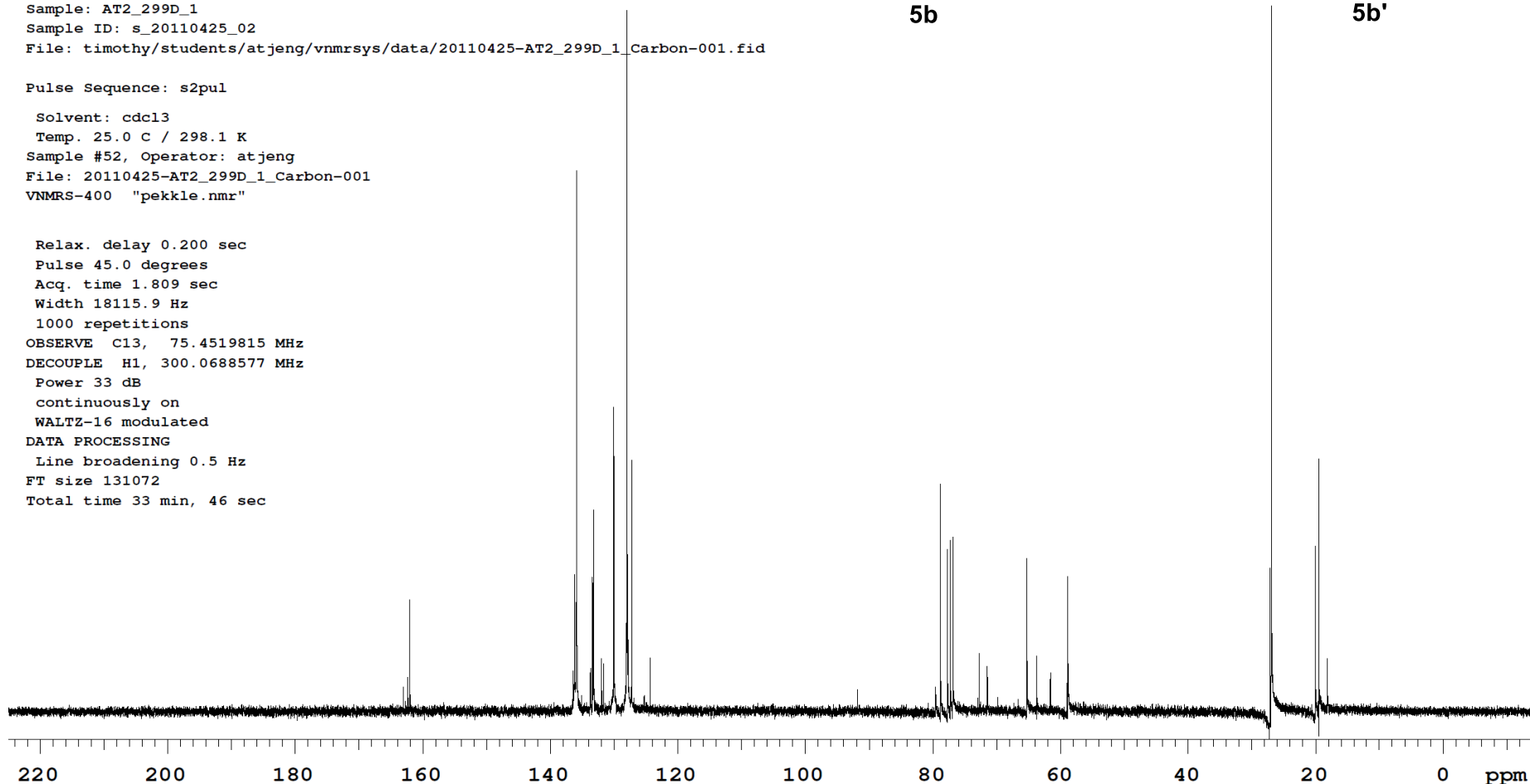


Sample: AT2_299D_1
Sample ID: s_20110425_02
File: timothy/students/atjeng/vnmrsys/data/20110425-AT2_299D_1_Carbon-001.fid

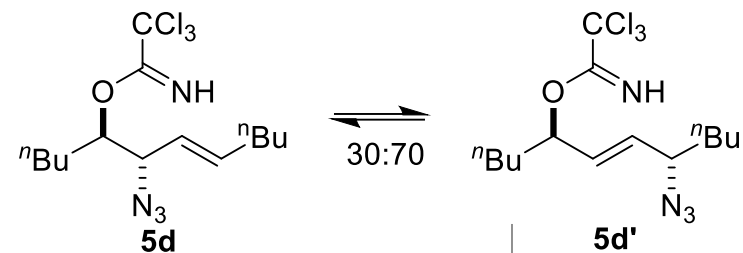
Pulse Sequence: s2pul

Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Sample #52, Operator: atjeng
File: 20110425-AT2_299D_1_Carbon-001
VNMRS-400 "pekkle.nmr"

Relax. delay 0.200 sec
Pulse 45.0 degrees
Acq. time 1.809 sec
Width 18115.9 Hz
1000 repetitions
OBSERVE C13, 75.4519815 MHz
DECOUPLE H1, 300.0688577 MHz
Power 33 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 33 min, 46 sec



^1H NMR of Compound 5d / 5d' (CDCl_3 ; 300 MHz)

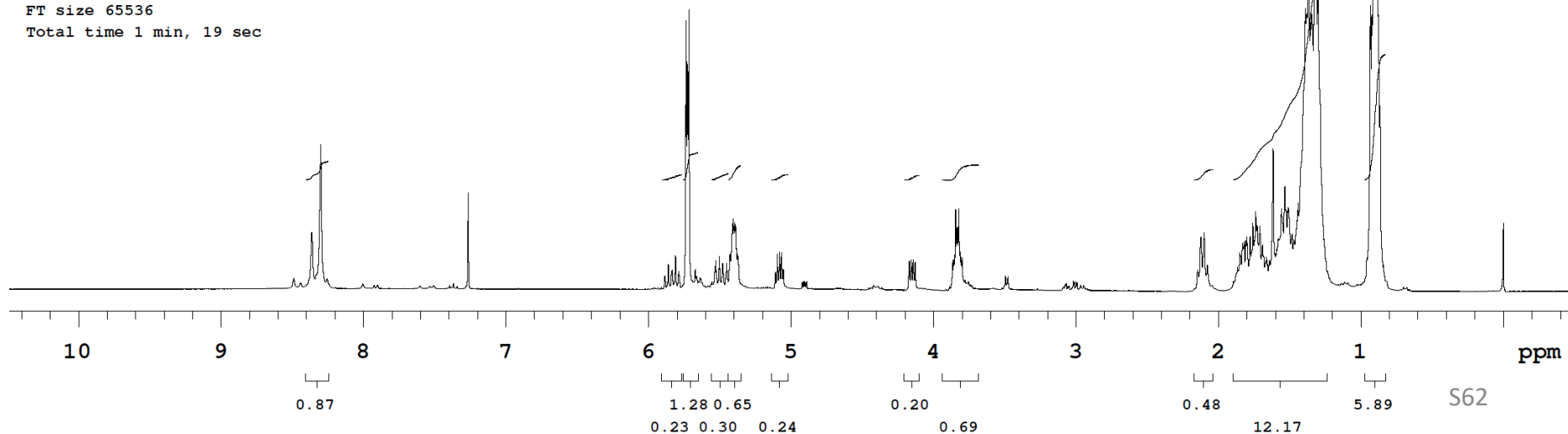


Sample: AT2_317B_2
Sample ID: s_20110616_02
File: timothy/students/atjeng/vnmrsys/data/20110616-AT2_317B_2_Proton-001.fid

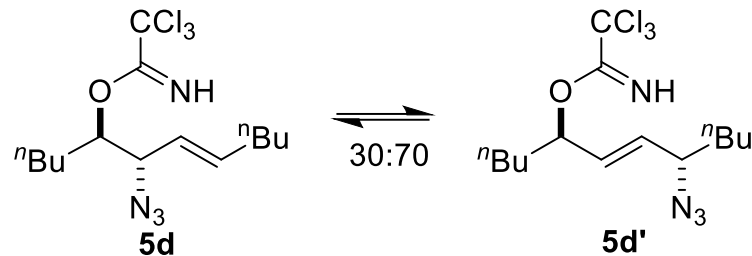
Pulse Sequence: s2pul

Solvent: cdcl_3
Temp. 25.0 C / 298.1 K
Sample #38, Operator: atjeng
File: 20110616-AT2_317B_2_Proton-001
VNMR-400 "pekkle.nmr"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 3.398 sec
Width 4800.8 Hz
16 repetitions
OBSERVE H1, 300.0673654 MHz
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 1 min, 19 sec



^{13}C NMR of Compound 5d / 5d' (CDCl_3 ; 100 MHz)

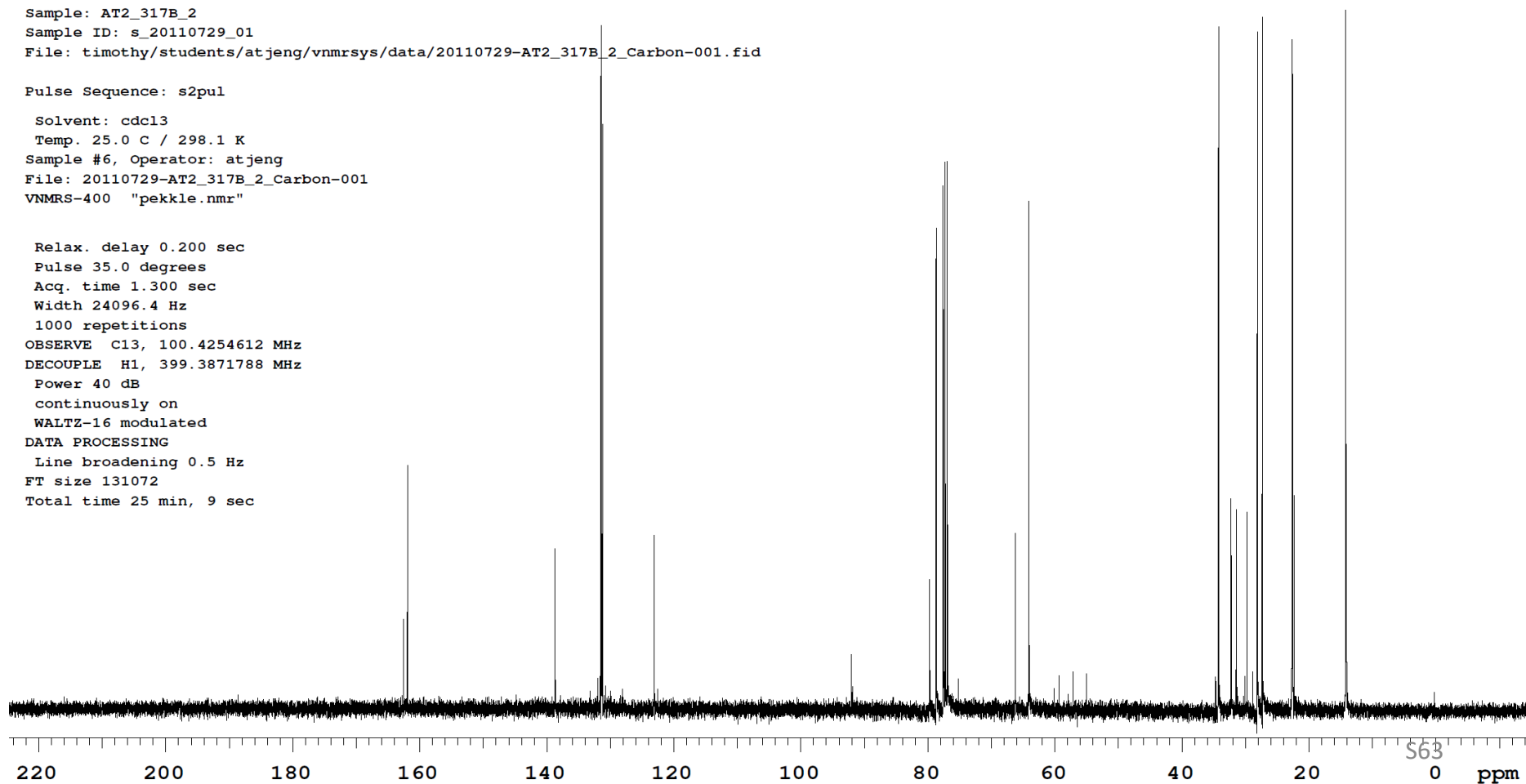


Sample: AT2_317B_2
Sample ID: s_20110729_01
File: timothy/students/atjeng/vnmrsys/data/20110729-AT2_317B_2_Carbon-001.fid

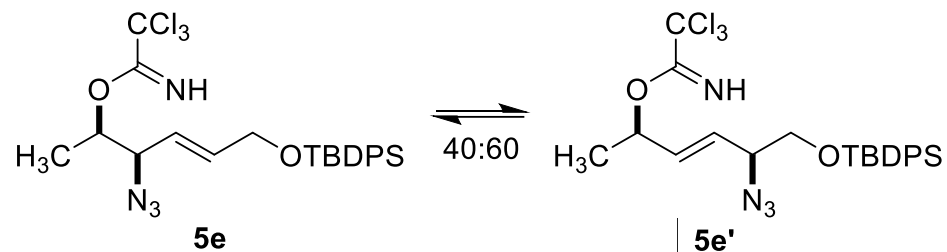
Pulse Sequence: s2pul

Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Sample #6, Operator: atjeng
File: 20110729-AT2_317B_2_Carbon-001
VNMRS-400 "pekkle.nmr"

Relax. delay 0.200 sec
Pulse 35.0 degrees
Acq. time 1.300 sec
Width 24096.4 Hz
1000 repetitions
OBSERVE C13, 100.4254612 MHz
DECOUPLE H1, 399.3871788 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 25 min, 9 sec



^1H NMR of Compound 5e / 5e' (CDCl_3 ; 400 MHz)

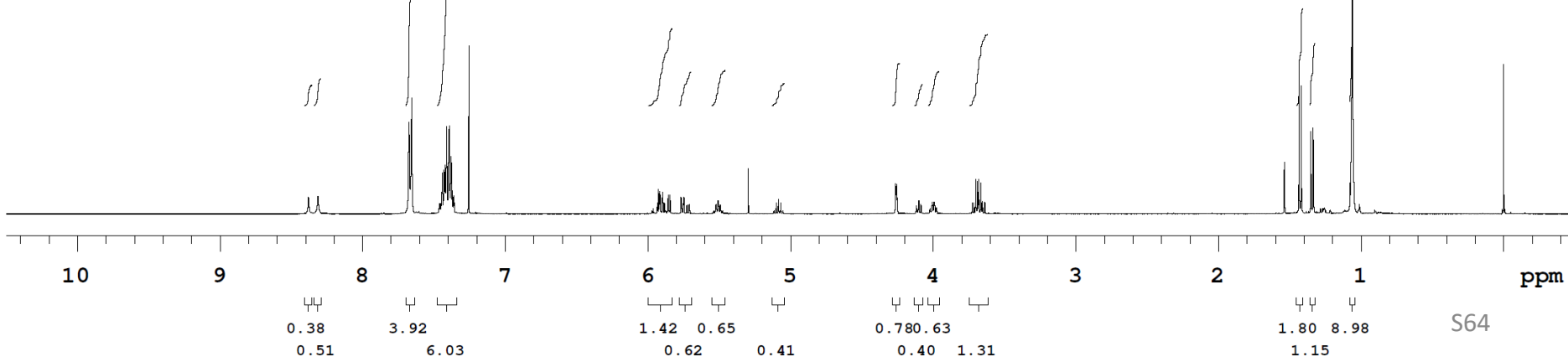


Sample: AT2_295_crude
Sample ID: s_20090129_95
File: timothy/students/atjeng/vnmrsys/data/20090130-AT2_295_crude_PROTON-002.fid

Pulse Sequence: s2pul

Solvent: cdcl_3
Temp. 25.0 C / 298.1 K
Sample #88, Operator: atjeng
File: 20090130-AT2_295_crude_PROTON-002
VNMR5-400 "pekkle.nmr"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.992 sec
Width 6398.0 Hz
16 repetitions
OBSERVE H1, 399.5395777 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 12 sec



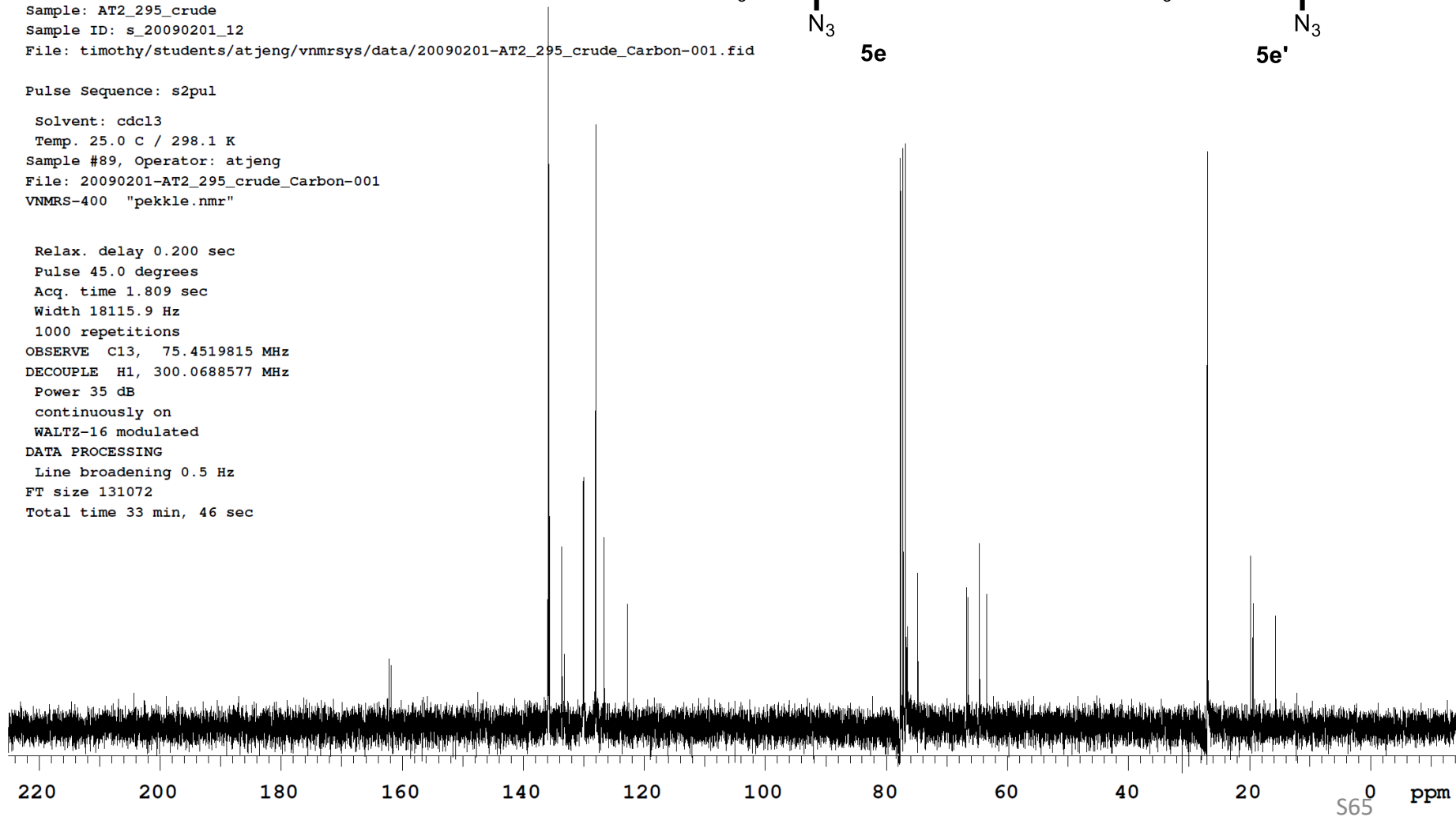
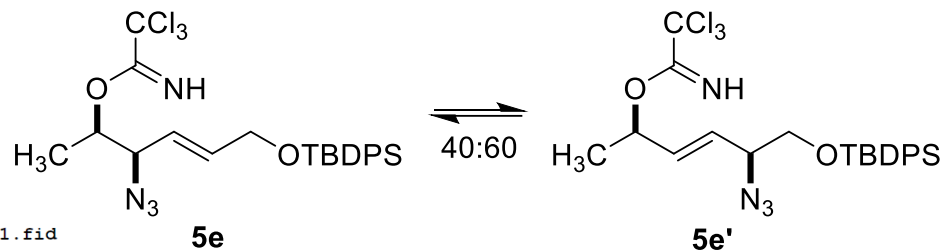
^{13}C NMR of Compound 5e / 5e' (CDCl_3 ; 75 MHz)

Sample: AT2_295_crude
Sample ID: s_20090201_12
File: timothy/students/atjeng/vnmrsys/data/20090201-AT2_295_crude_Carbon-001.fid

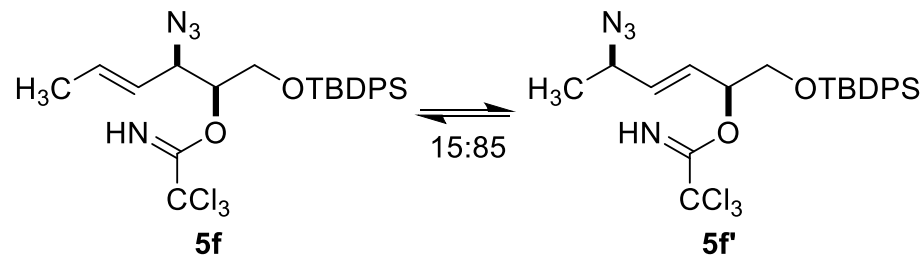
Pulse Sequence: s2pul

Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Sample #89, Operator: atjeng
File: 20090201-AT2_295_crude_Carbon-001
VNMR5-400 "pekkle.nmr"

Relax. delay 0.200 sec
Pulse 45.0 degrees
Acq. time 1.809 sec
Width 18115.9 Hz
1000 repetitions
OBSERVE C13, 75.4519815 MHz
DECOUPLE H1, 300.0688577 MHz
Power 35 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 33 min, 46 sec



¹H NMR of Compound 5f / 5f' (CDCl₃; 400 MHz)

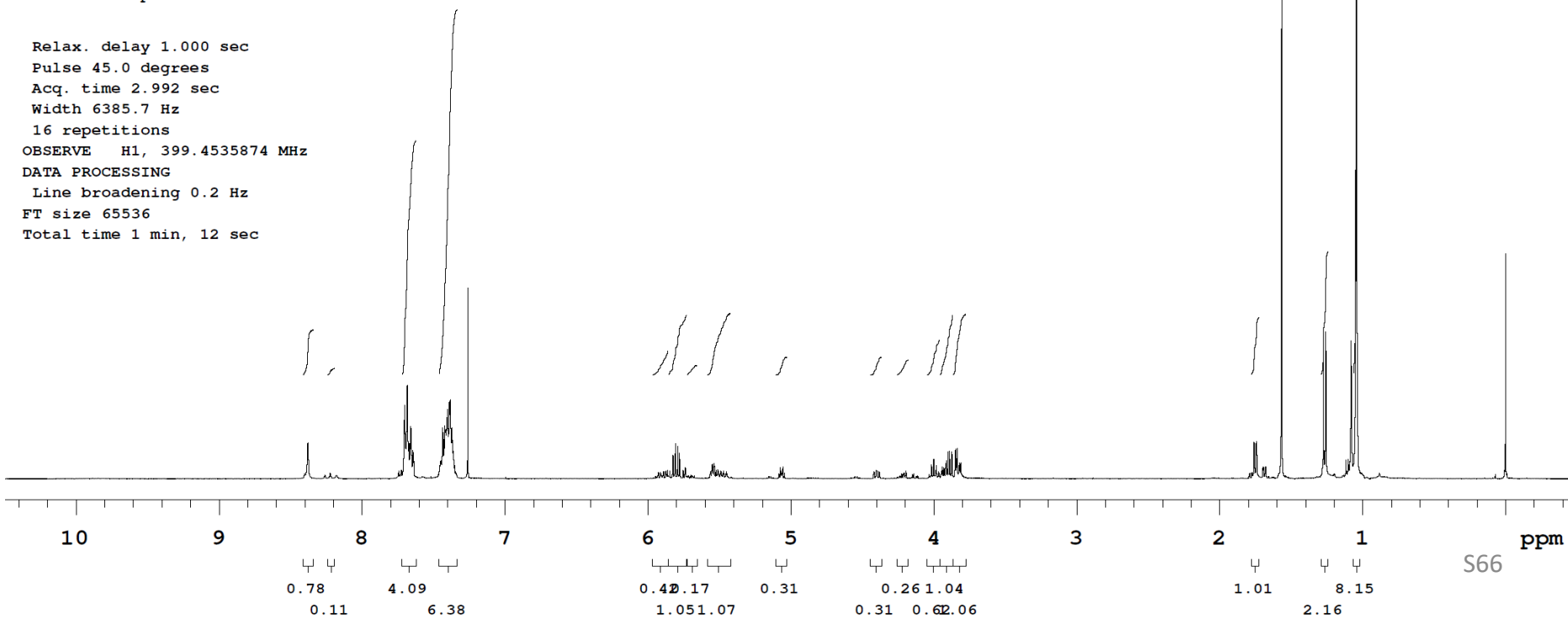


Sample: AT2_440B_crude
Sample ID: s_20100818_65
File: timothy/students/atjeng/vnmrsys/data/20100818-AT2_440B_crude_Proton-002.fid

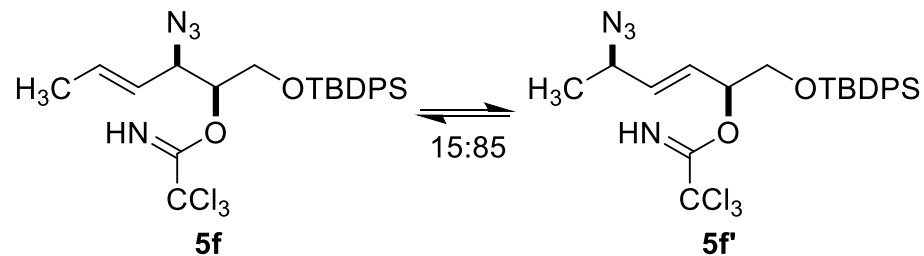
Pulse Sequence: s2pul

Solvent: cdc13
Temp. 25.0 C / 298.1 K
Sample #62, Operator: atjeng
File: 20100818-AT2_440B_crude_Proton-002
VNMR-400 "pekkle.nmr"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.992 sec
Width 6385.7 Hz
16 repetitions
OBSERVE H1, 399.4535874 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 12 sec



^{13}C NMR of Compound 5f / 5f' (CDCl_3 ; 75 MHz)

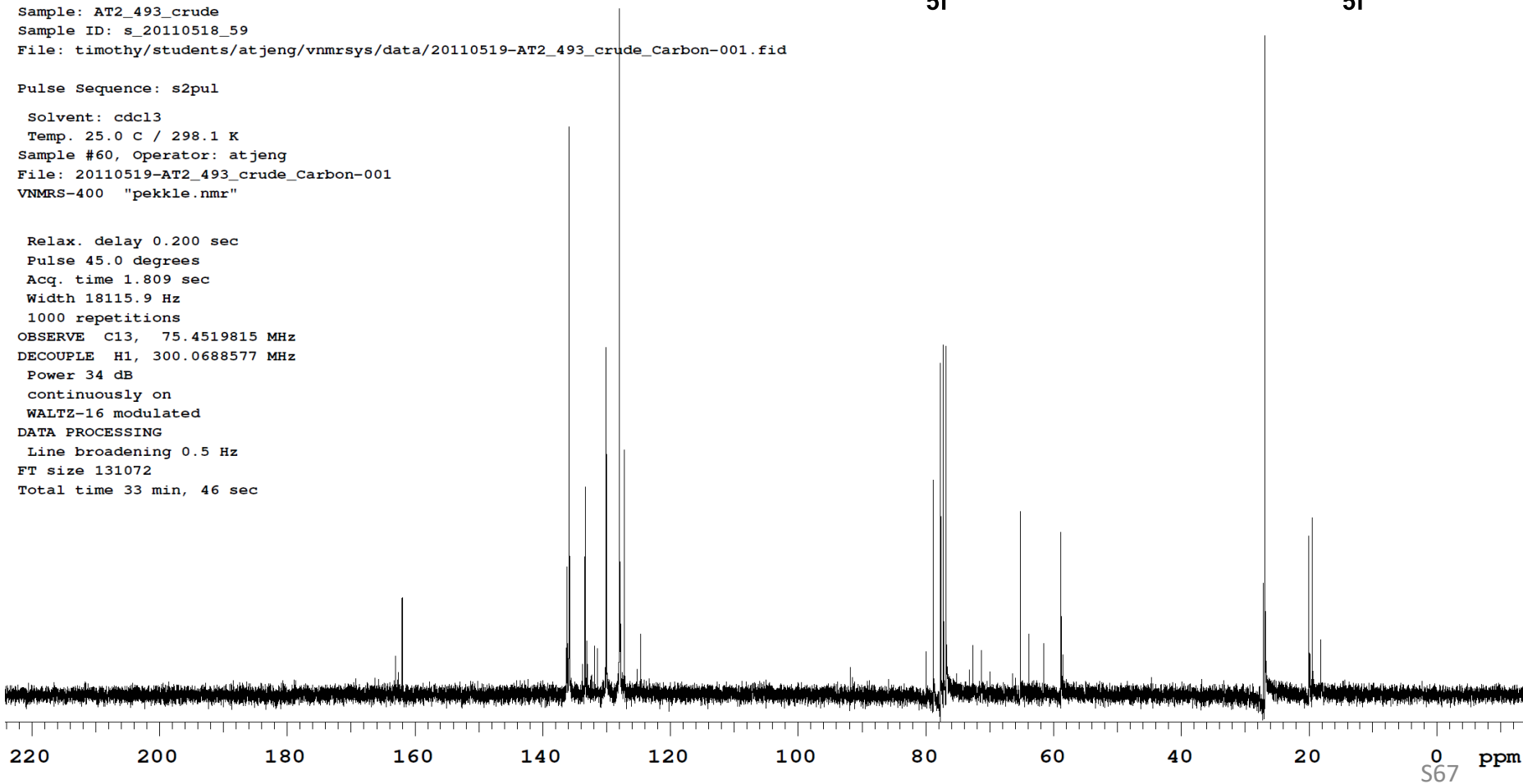


Sample: AT2_493_crude
Sample ID: s_20110518_59
File: timothy/students/atjeng/vnmrsys/data/20110519-AT2_493_crude_Carbon-001.fid

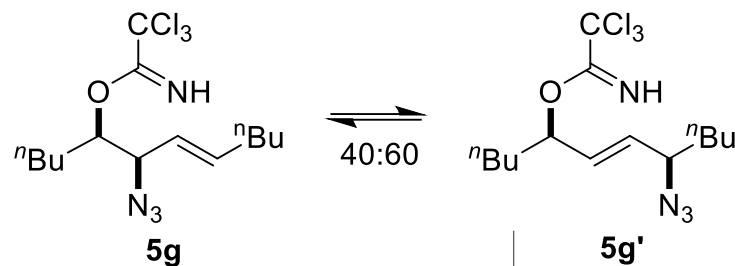
Pulse Sequence: s2pul

Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Sample #60, Operator: atjeng
File: 20110519-AT2_493_crude_Carbon-001
VNMR-400 "pekkle.nmr"

Relax. delay 0.200 sec
Pulse 45.0 degrees
Acq. time 1.809 sec
Width 18115.9 Hz
1000 repetitions
OBSERVE C13, 75.4519815 MHz
DECOUPLE H1, 300.0688577 MHz
Power 34 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 33 min, 46 sec



^1H NMR of Compound 5g / 5g' (CDCl_3 ; 400 MHz)

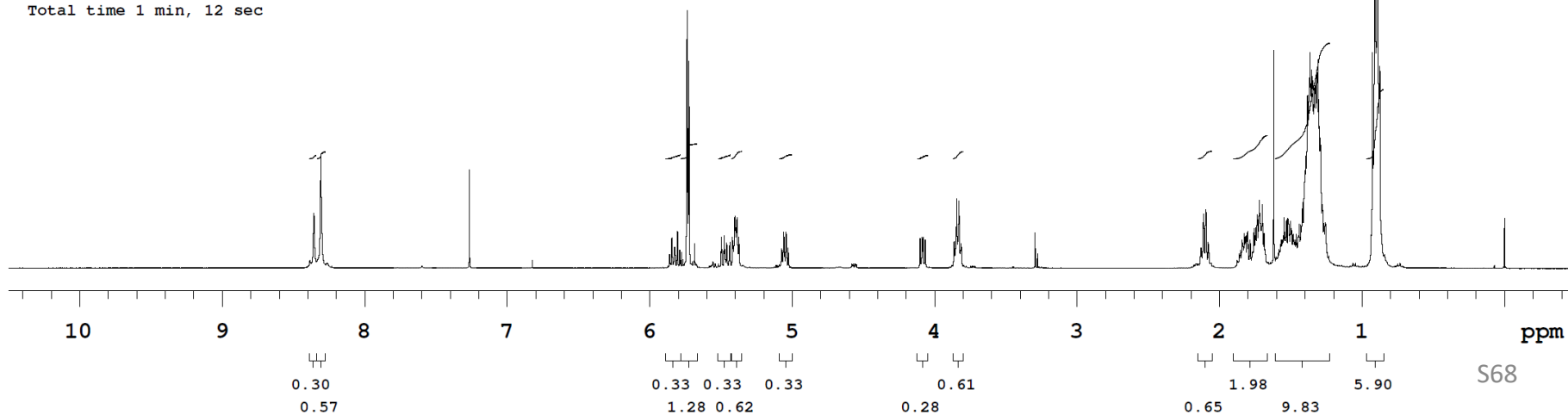


Sample: AT2_456B_1
Sample ID: s_20110627_01
File: timothy/students/atjeng/vnmrsys/data/20110627-AT2_456B_1_Proton-002.fid

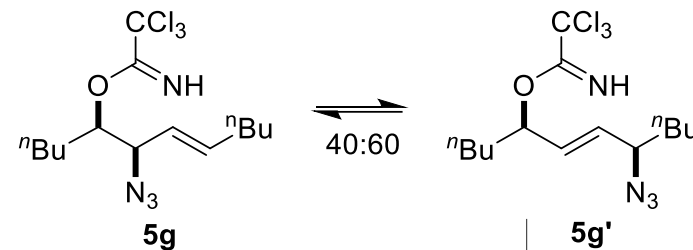
Pulse Sequence: s2pul

Solvent: cdc13
Temp. 25.0 C / 298.1 K
Sample #86, Operator: atjeng
File: 20110627-AT2_456B_1_Proton-002
VNMR-400 "pekkle.nmr"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.992 sec
Width 6385.7 Hz
16 repetitions
OBSERVE H1, 399.3851842 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 12 sec



^{13}C NMR of Compound 5g / 5g' (CDCl_3 ; 100 MHz)

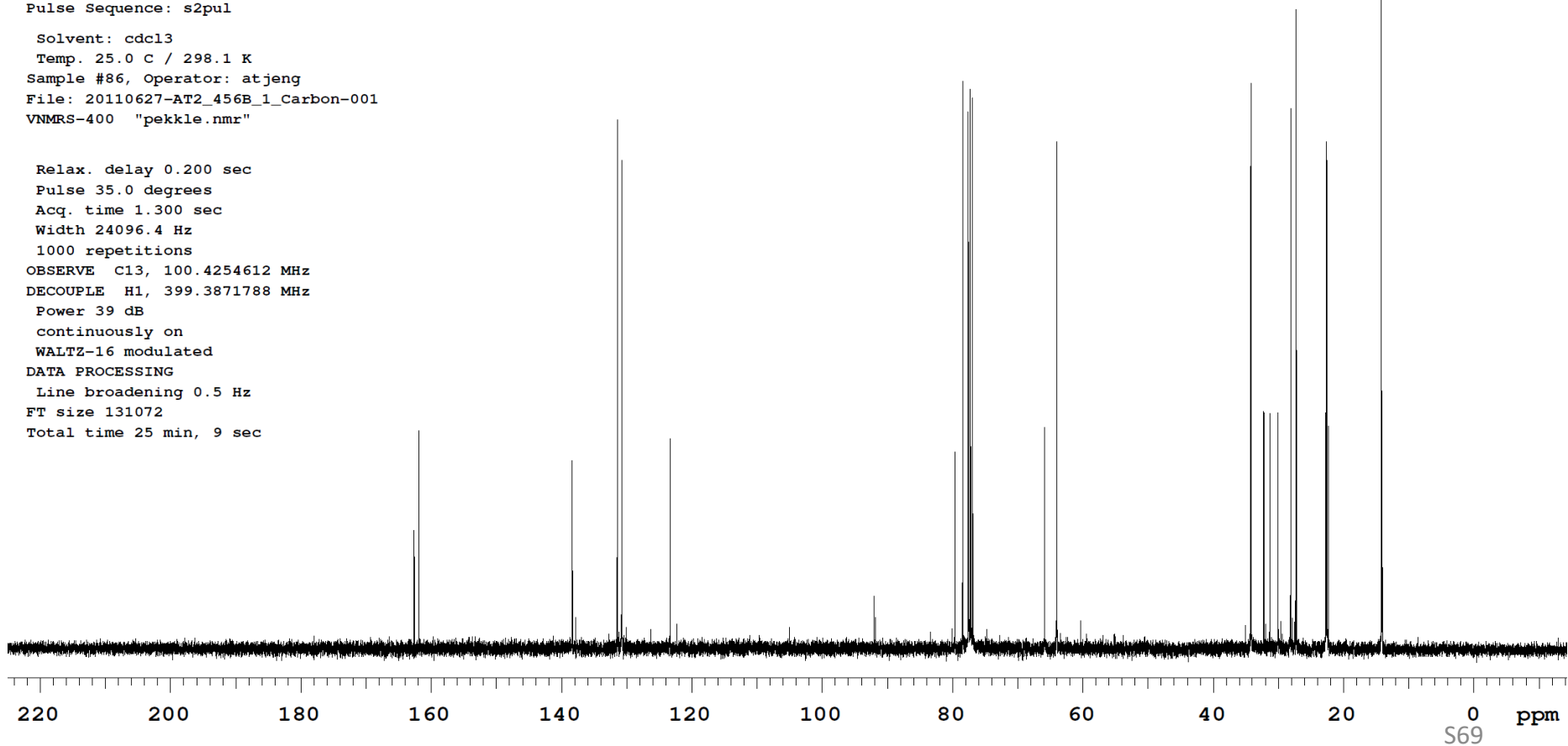


Sample: AT2_456B_1
Sample ID: s_20110627_01
File: timothy/students/atjeng/vnmrsys/data/20110627-AT2_456B_1_Carbon-001.fid

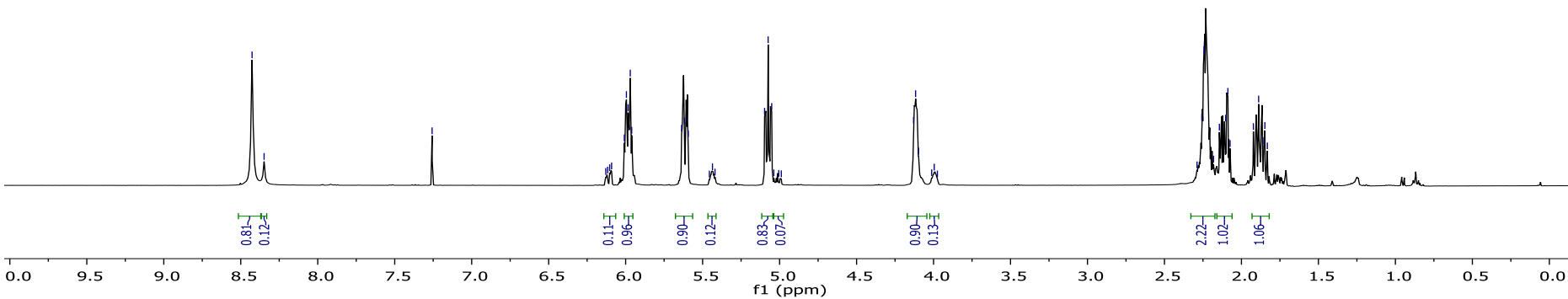
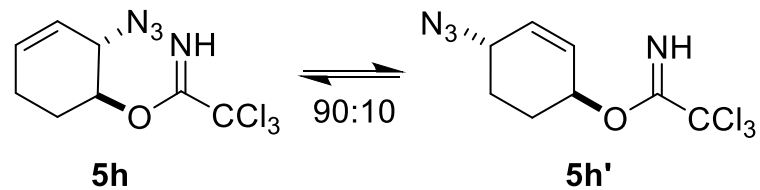
Pulse Sequence: s2pul

Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Sample #86, Operator: atjeng
File: 20110627-AT2_456B_1_Carbon-001
VNMRS-400 "pekkle.nmr"

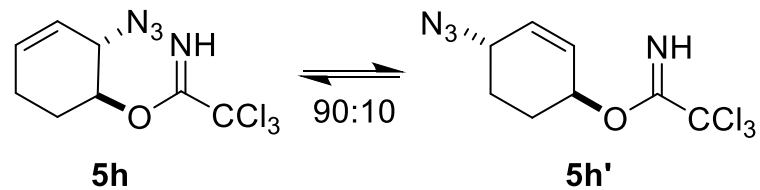
Relax. delay 0.200 sec
Pulse 35.0 degrees
Acq. time 1.300 sec
Width 24096.4 Hz
1000 repetitions
OBSERVE c13, 100.4254612 MHz
DECOUPLE H1, 399.3871788 MHz
Power 39 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 25 min, 9 sec



^1H NMR of Compound 5h / 5h' (CDCl_3 ; 400 MHz)



^{13}C NMR of Compound 5h / 5h' (CDCl_3 ; 100 MHz)



161.99
161.85

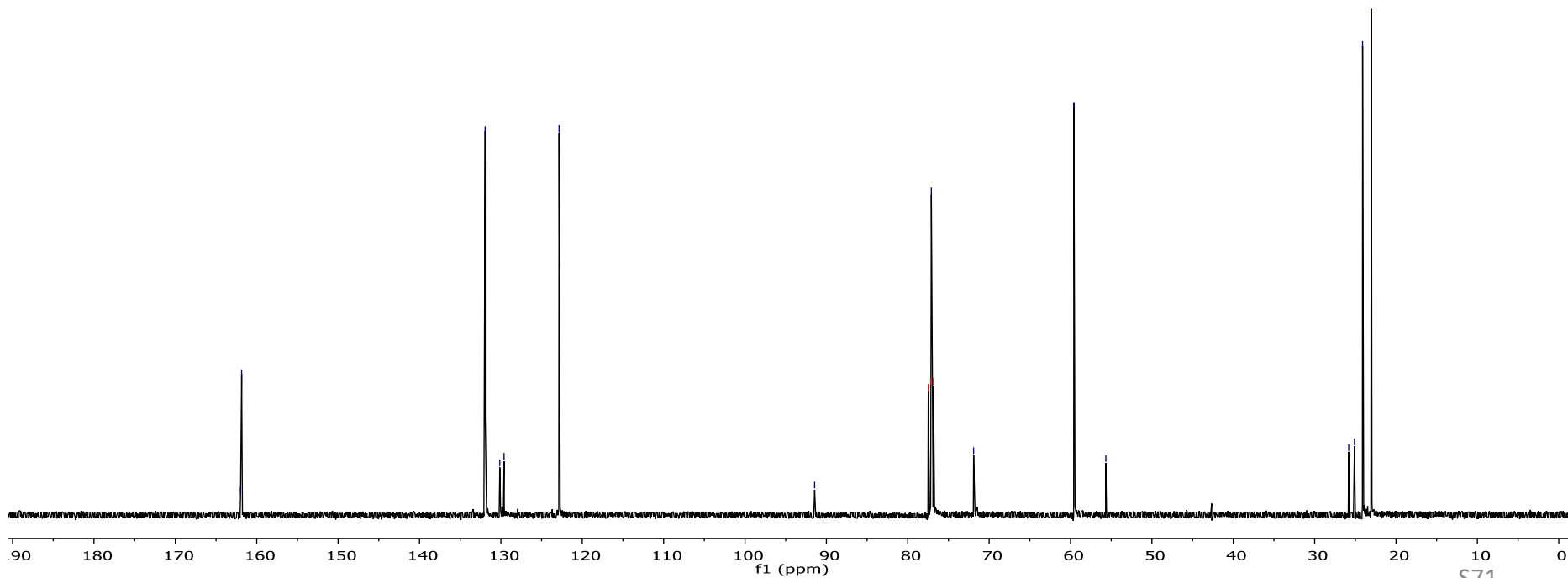
131.93
130.13
129.61
122.85

91.45

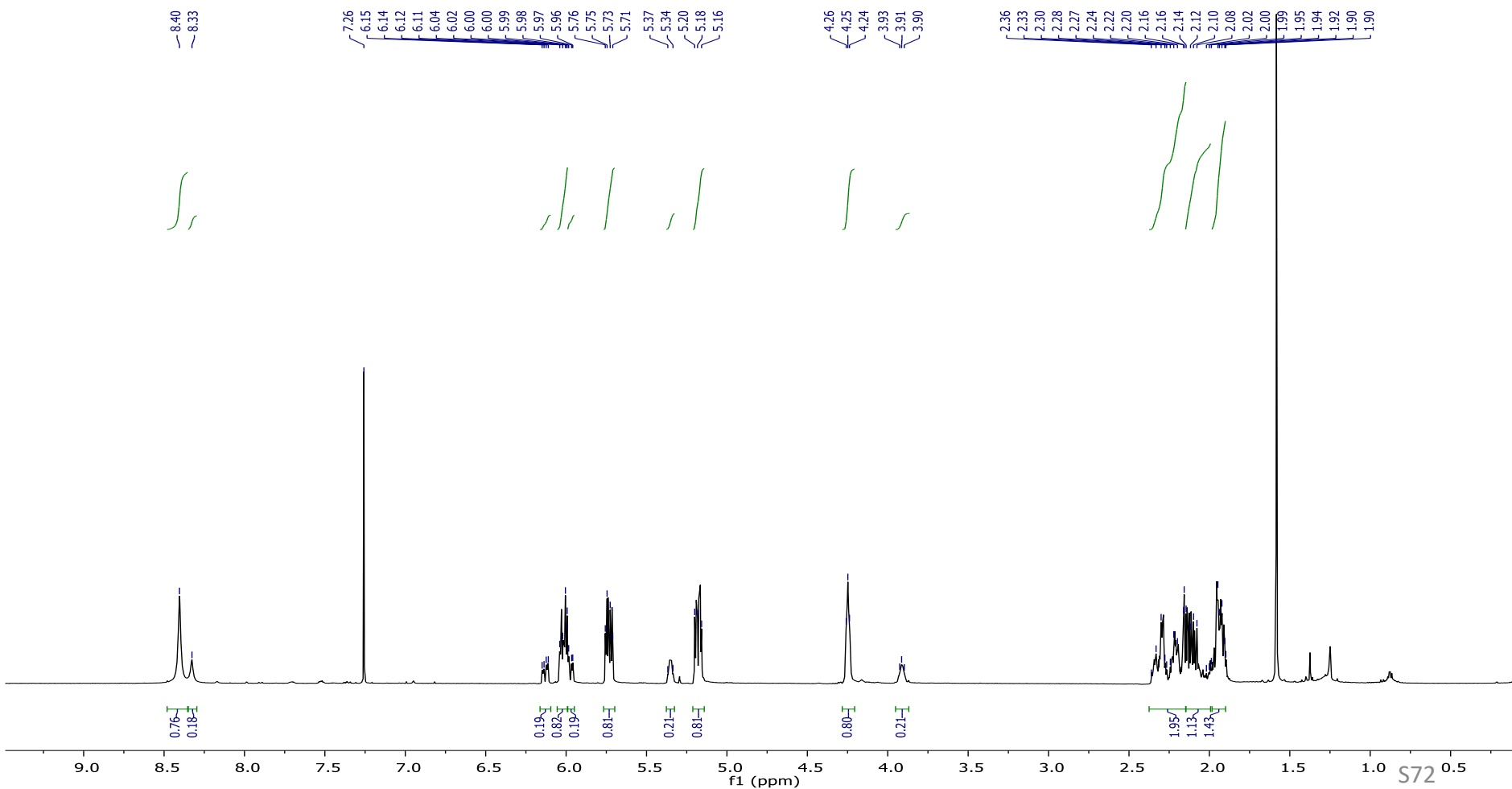
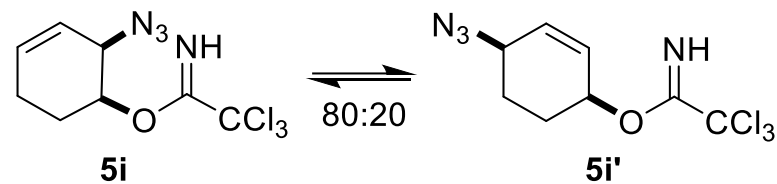
77.48 cdd3
77.16 cdd3
77.10
76.84 cdd3
71.91

59.58
55.66

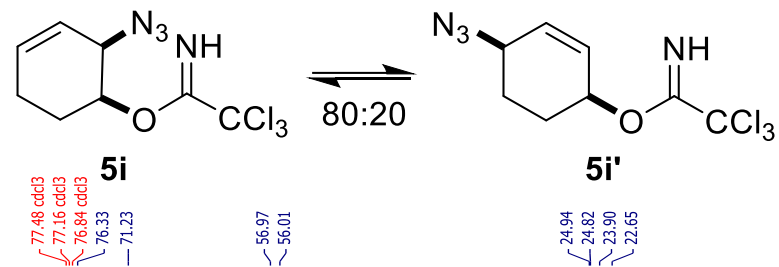
25.81
25.11
24.11
23.03



^1H NMR of Compound 5i / 5i' (CDCl_3 ; 400 MHz)



^{13}C NMR of Compound 5i / 5i' (CDCl_3 ; 100 MHz)



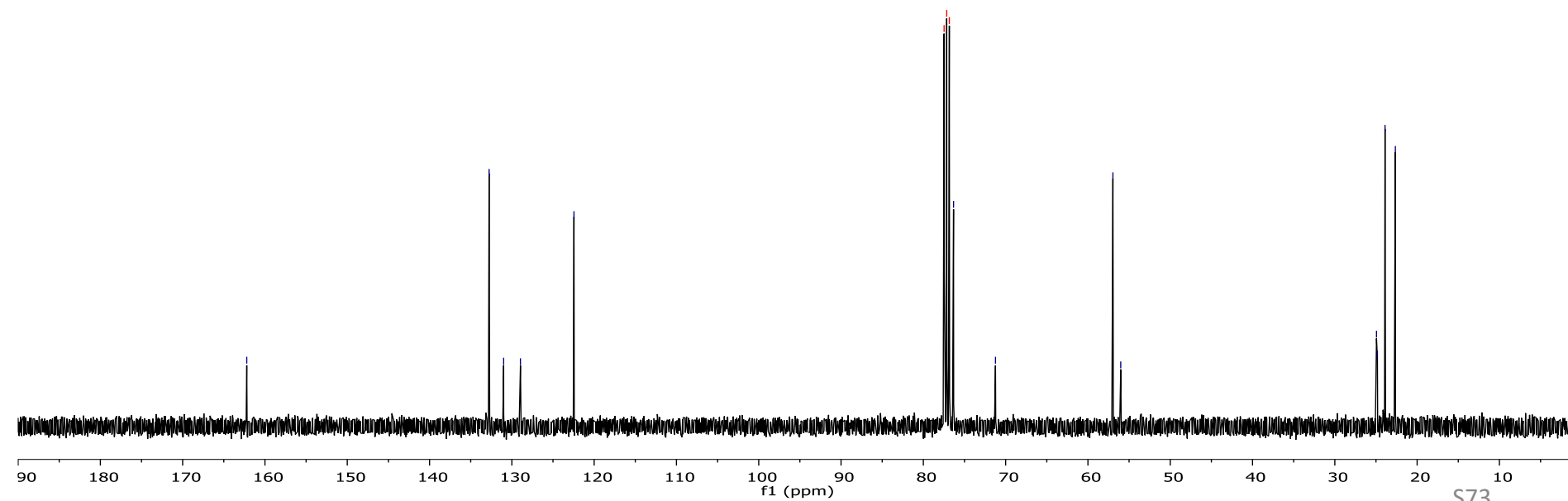
162.21

132.77

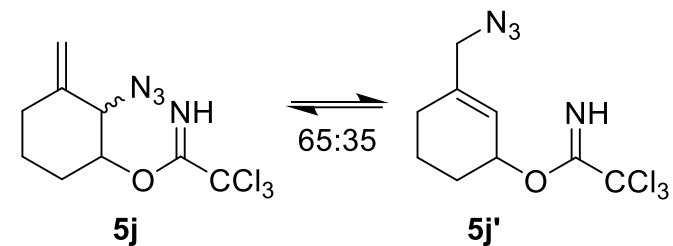
131.00

128.96

122.45



¹H NMR of Compound 5j / 5j' (CDCl₃; 400 MHz)

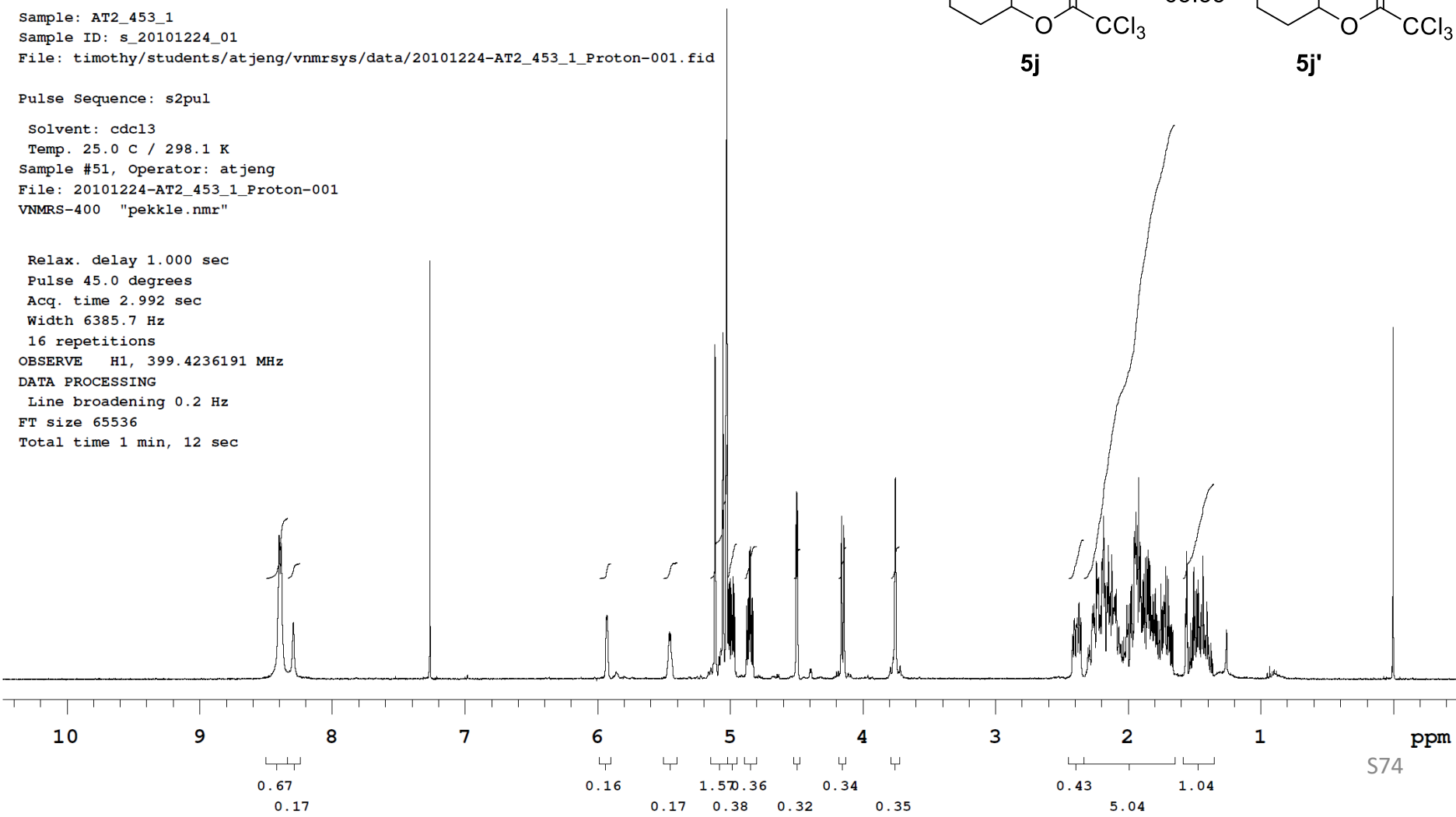


Sample: AT2_453_1
Sample ID: s_20101224_01
File: timothy/students/atjeng/vnmrsys/data/20101224-AT2_453_1_Proton-001.fid

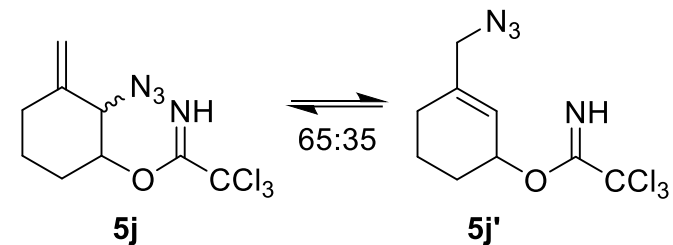
Pulse Sequence: s2pul

Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Sample #51, Operator: atjeng
File: 20101224-AT2_453_1_Proton-001
VNMR-400 "pekkle.nmr"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.992 sec
Width 6385.7 Hz
16 repetitions
OBSERVE H1, 399.4236191 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 12 sec



^{13}C NMR of Compound 5j / 5j' (CDCl_3 ; 100 MHz)

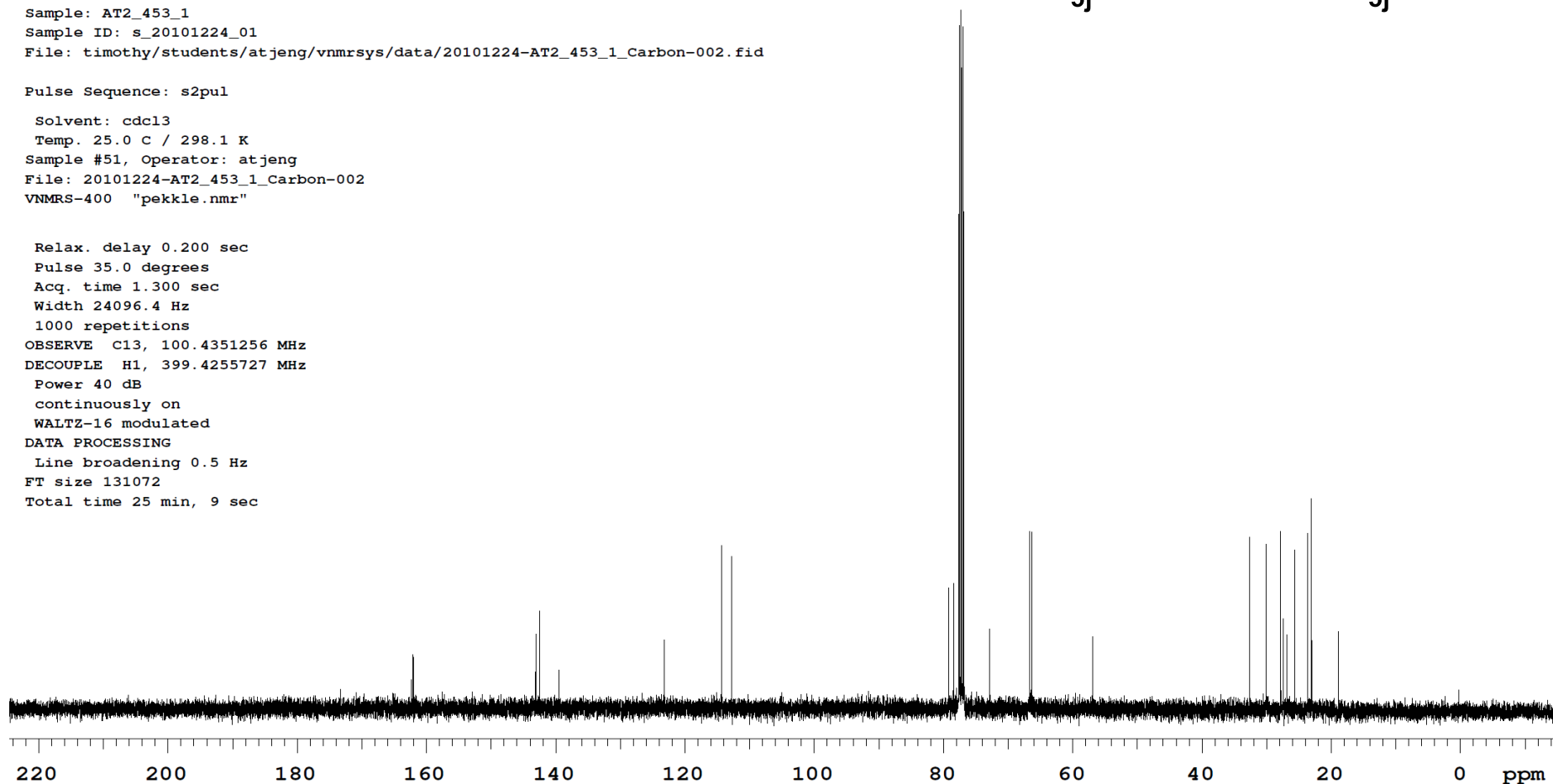


Sample: AT2_453_1
Sample ID: s_20101224_01
File: timothy/students/atjeng/vnmrsys/data/20101224-AT2_453_1_Carbon-002.fid

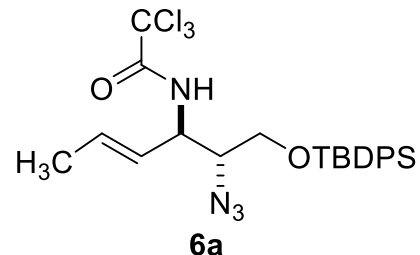
Pulse Sequence: s2pul

Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Sample #51, Operator: atjeng
File: 20101224-AT2_453_1_Carbon-002
VNMR-400 "pekkle.nmr"

Relax. delay 0.200 sec
Pulse 35.0 degrees
Acq. time 1.300 sec
Width 24096.4 Hz
1000 repetitions
OBSERVE C13, 100.4351256 MHz
DECOUPLE H1, 399.4255727 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 25 min, 9 sec



^1H NMR of Compound 6a (CDCl_3 ; 400 MHz)



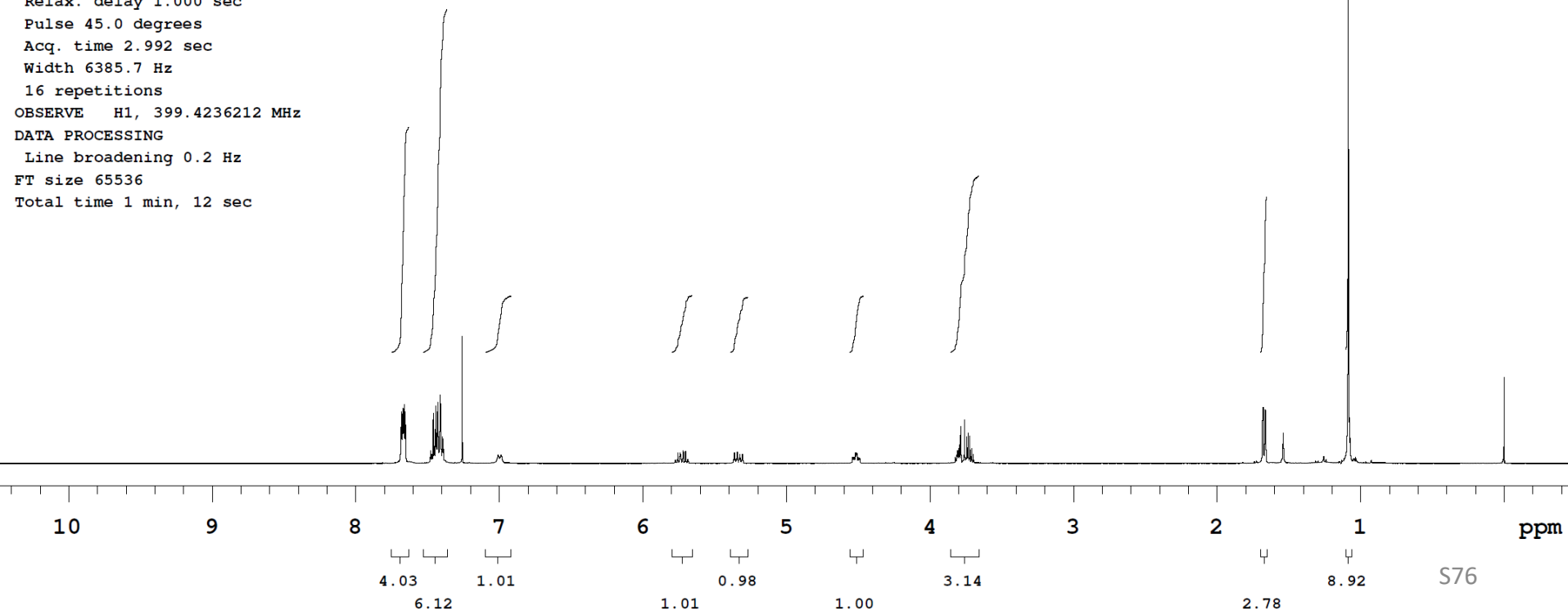
VARIAN 

Sample: AT2_m289_
Sample ID: s_20101224_05
File: timothy/students/atjeng/vnmrsys/data/20101224-AT2_m289__Proton-002.fid

Pulse Sequence: s2pul

Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Sample #55, Operator: atjeng
File: 20101224-AT2_m289__Proton-002
VNMR5-400 "pekkle.nmr"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.992 sec
Width 6385.7 Hz
16 repetitions
OBSERVE H1, 399.4236212 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 12 sec



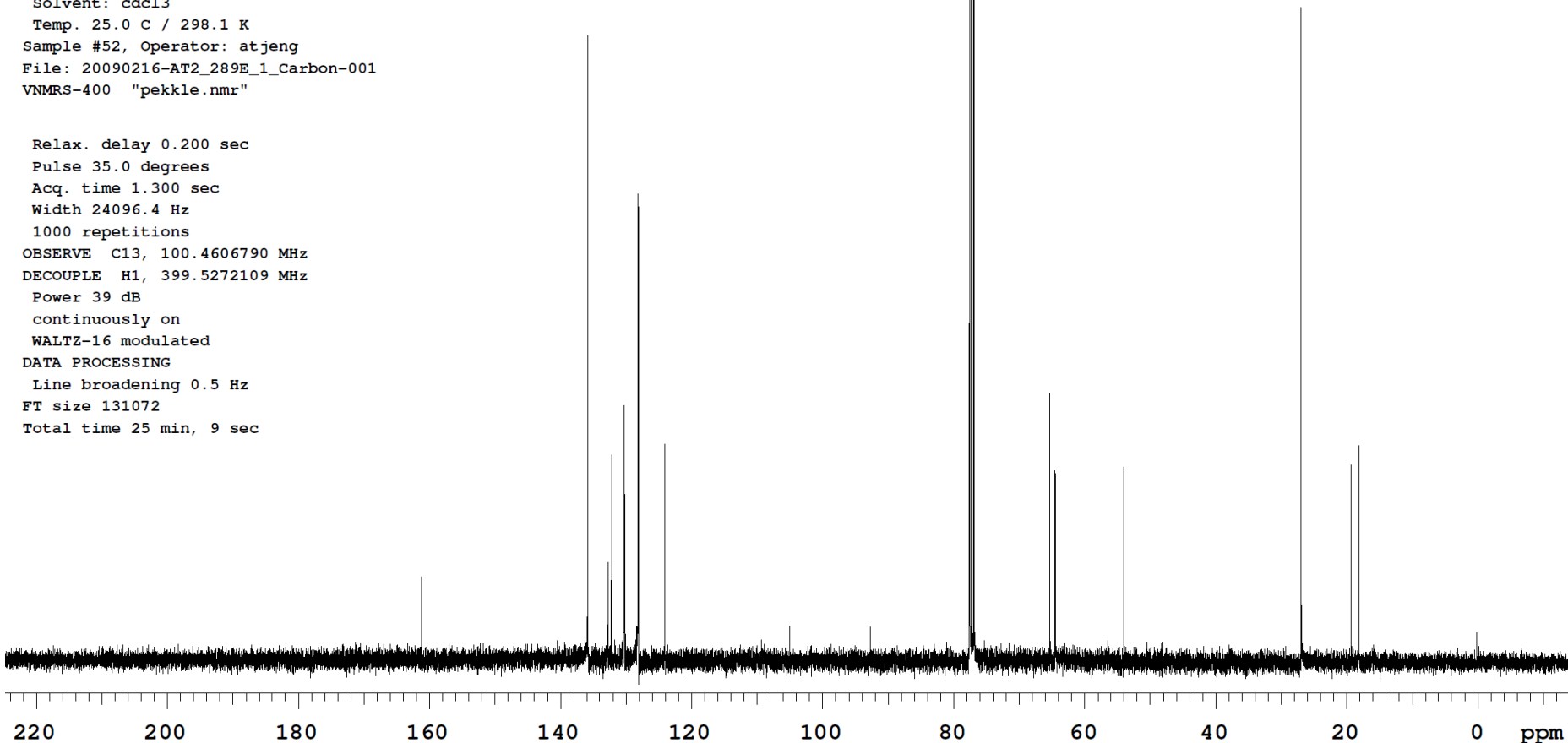
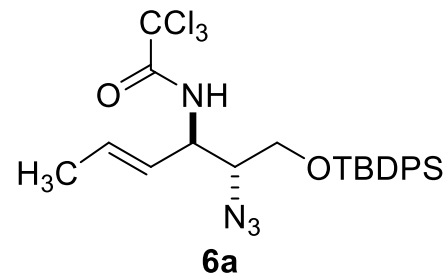
^{13}C NMR of Compound 6a (CDCl_3 ; 100 MHz)

Sample: AT2_289E_1
Sample ID: s_20090215_24
File: timothy/students/atjeng/vnmrsys/data/20090216-AT2_289E_1_Carbon-001.fid

Pulse Sequence: s2pul

Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Sample #52, Operator: atjeng
File: 20090216-AT2_289E_1_Carbon-001
VNMRS-400 "pekkle.nmr"

Relax. delay 0.200 sec
Pulse 35.0 degrees
Acq. time 1.300 sec
Width 24096.4 Hz
1000 repetitions
OBSERVE C13, 100.4606790 MHz
DECOUPLE H1, 399.5272109 MHz
Power 39 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 25 min, 9 sec



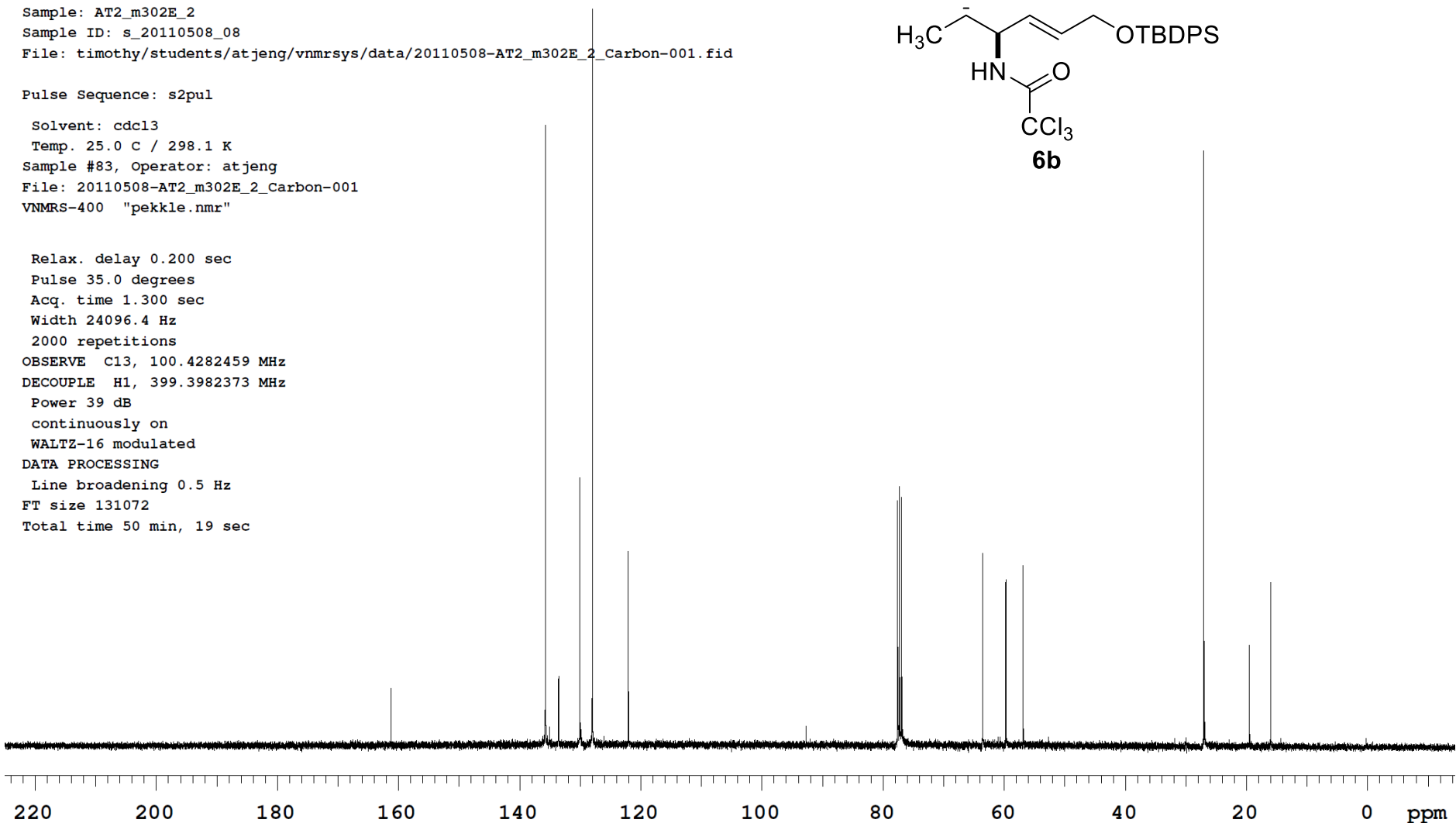
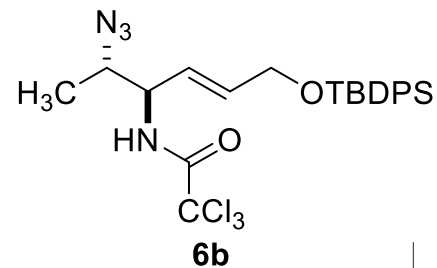
^{13}C NMR of Compound 6b (CDCl_3 ; 100 MHz)

Sample: AT2_m302E_2
Sample ID: s_20110508_08
File: timothy/students/atjeng/vnmrsys/data/20110508-AT2_m302E_2_Carbon-001.fid

Pulse Sequence: s2pul

Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Sample #83, Operator: atjeng
File: 20110508-AT2_m302E_2_Carbon-001
VNMRS-400 "pekkle.nmr"

Relax. delay 0.200 sec
Pulse 35.0 degrees
Acq. time 1.300 sec
Width 24096.4 Hz
2000 repetitions
OBSERVE C13, 100.4282459 MHz
DECOUPLE H1, 399.3982373 MHz
Power 39 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 50 min, 19 sec



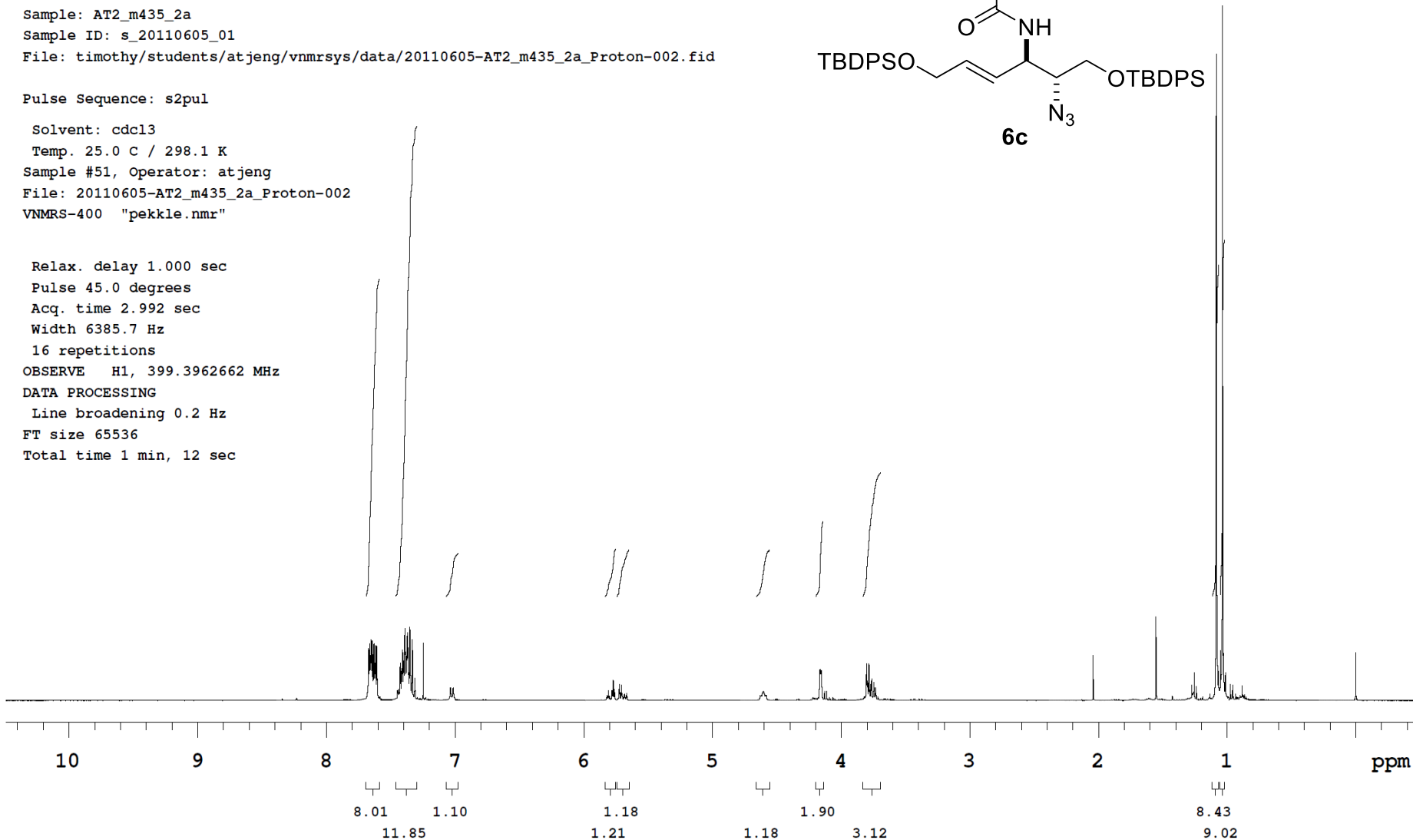
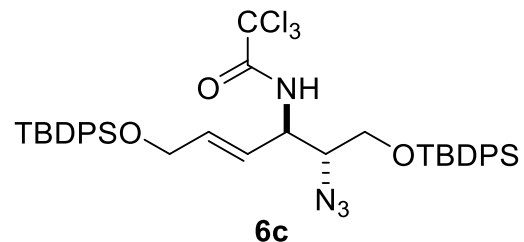
^1H NMR of Compound 6c (CDCl_3 ; 400 MHz)

Sample: AT2_m435_2a
Sample ID: s_20110605_01
File: timothy/students/atjeng/vnmrsys/data/20110605-AT2_m435_2a_Proton-002.fid

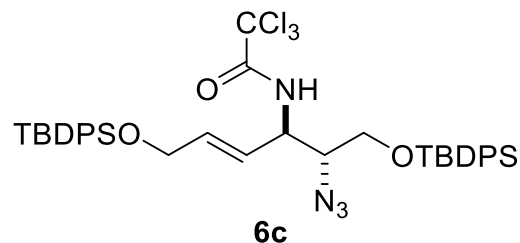
Pulse Sequence: s2pul

Solvent: cdc13
Temp. 25.0 C / 298.1 K
Sample #51, Operator: atjeng
File: 20110605-AT2_m435_2a_Proton-002
VNMR-400 "pekkle.nmr"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.992 sec
Width 6385.7 Hz
16 repetitions
OBSERVE H1, 399.3962662 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 12 sec



^{13}C NMR of Compound 6c (CDCl_3 ; 100 MHz)

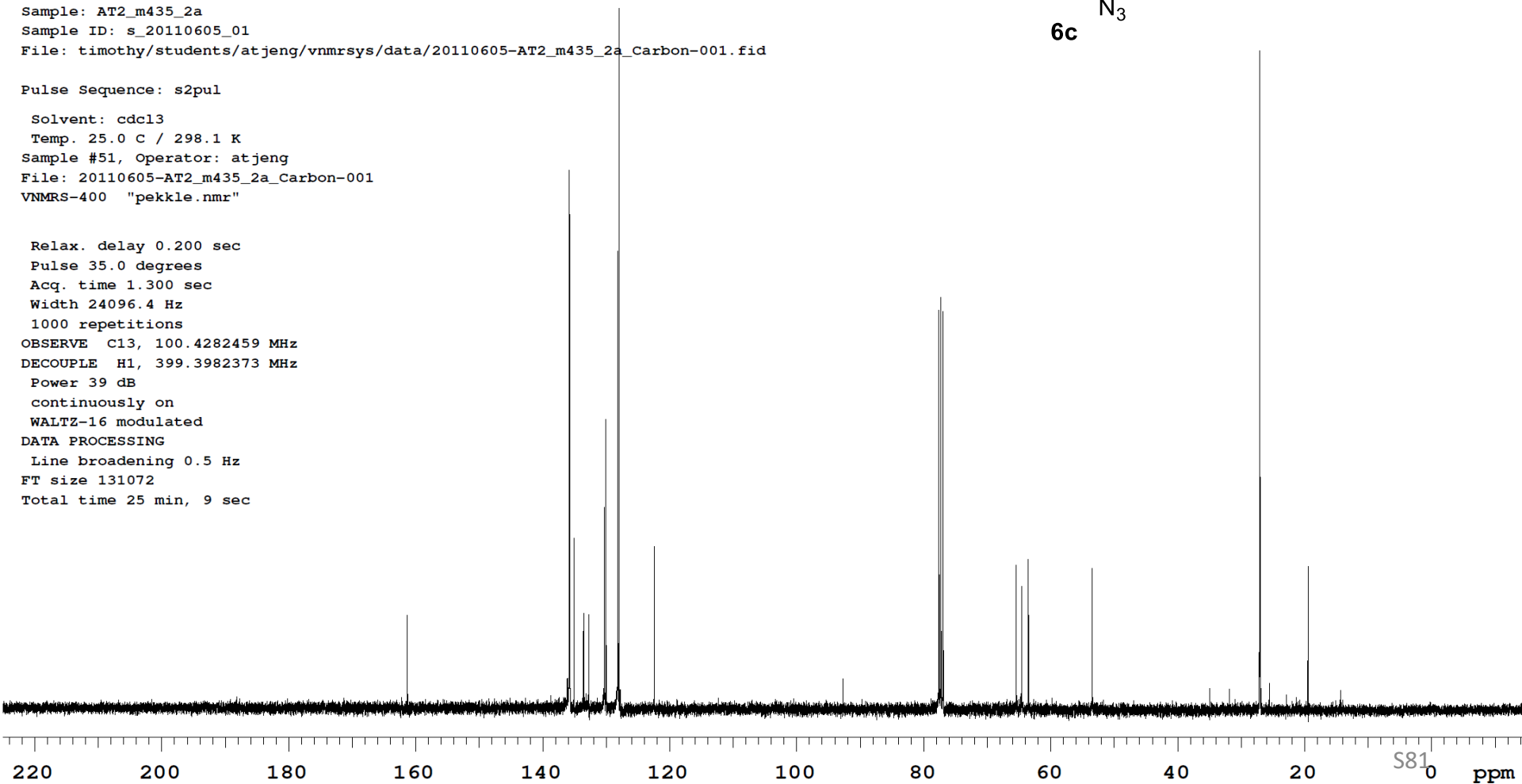


Sample: AT2_m435_2a
Sample ID: s_20110605_01
File: timothy/students/atjeng/vnmrsys/data/20110605-AT2_m435_2a_Carbon-001.fid

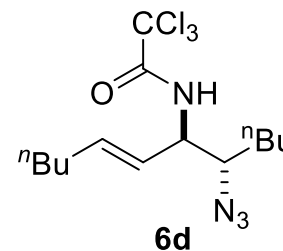
Pulse Sequence: s2pul

Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Sample #51, Operator: atjeng
File: 20110605-AT2_m435_2a_Carbon-001
VNMRS-400 "pekkle.nmr"

Relax. delay 0.200 sec
Pulse 35.0 degrees
Acq. time 1.300 sec
Width 24096.4 Hz
1000 repetitions
OBSERVE C13, 100.4282459 MHz
DECOUPLE H1, 399.3982373 MHz
Power 39 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 25 min, 9 sec



^1H NMR of Compound 6d (CDCl_3 ; 300 MHz)

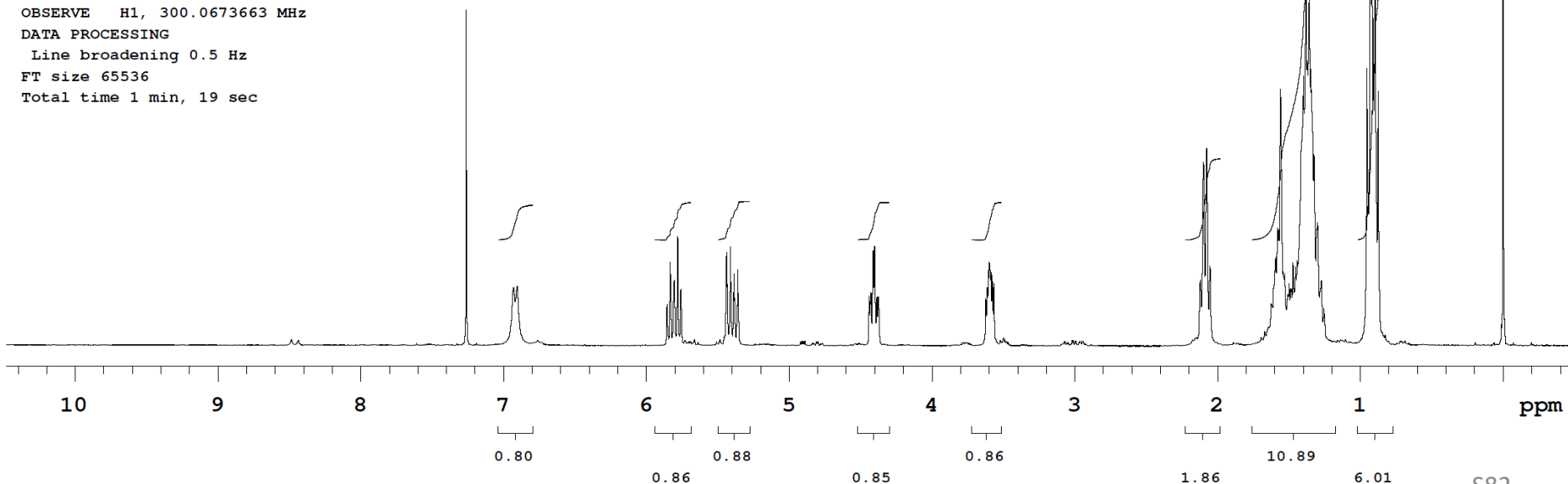


Sample: AT2_m333_1
Sample ID: s_20090723_02
File: timothy/students/atjeng/vnmrsys/data/20090723-AT2_m333_1_Proton-001.fid

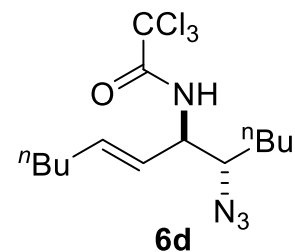
Pulse Sequence: s2pul

Solvent: cdc13
Temp. 25.0 C / 298.1 K
Sample #85, Operator: atjeng
File: 20090723-AT2_m333_1_Proton-001
VNMR-400 "pekkle.nmr"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 3.396 sec
Width 4803.1 Hz
16 repetitions
OBSERVE H1, 300.0673663 MHz
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 1 min, 19 sec



^{13}C NMR of Compound 6d (CDCl_3 ; 75 MHz)

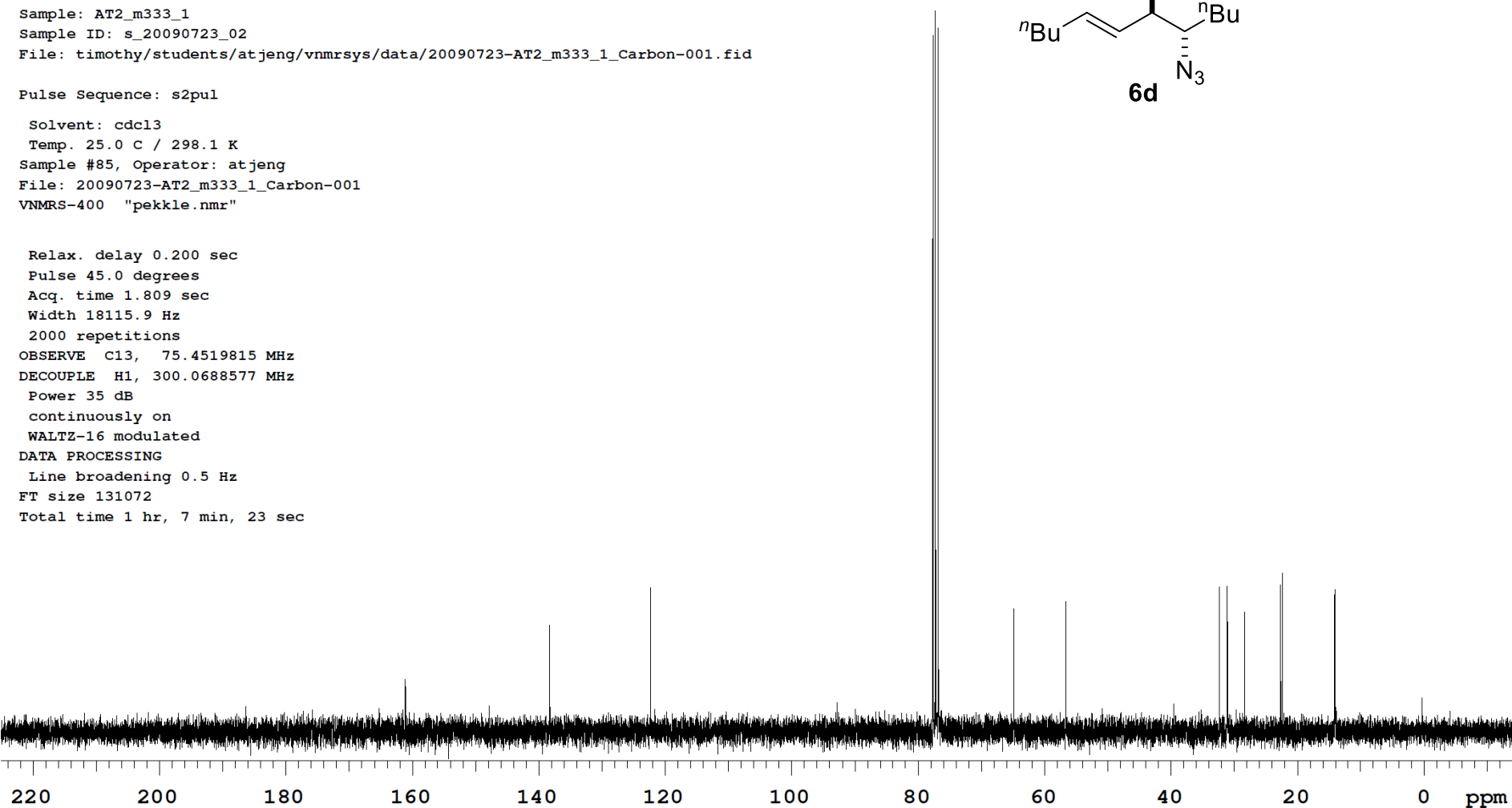


Sample: AT2_m333_1
Sample ID: s_20090723_02
File: timothy/students/atjeng/vnmrsys/data/20090723-AT2_m333_1_Carbon-001.fid

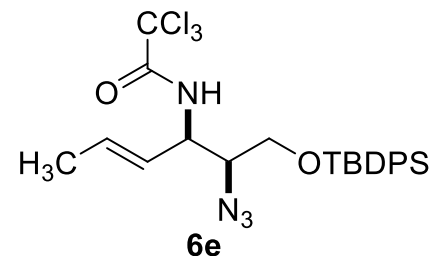
Pulse Sequence: s2pul

Solvent: cdc13
Temp. 25.0 C / 298.1 K
Sample #85, Operator: atjeng
File: 20090723-AT2_m333_1_Carbon-001
VNMRS-400 "pekkle.nmr"

Relax. delay 0.200 sec
Pulse 45.0 degrees
Acq. time 1.809 sec
Width 18115.9 Hz
2000 repetitions
OBSERVE C13, 75.4519815 MHz
DECOUPLE H1, 300.0688577 MHz
Power 35 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 1 hr, 7 min, 23 sec



^1H NMR of Compound 6e (CDCl_3 ; 300 MHz)

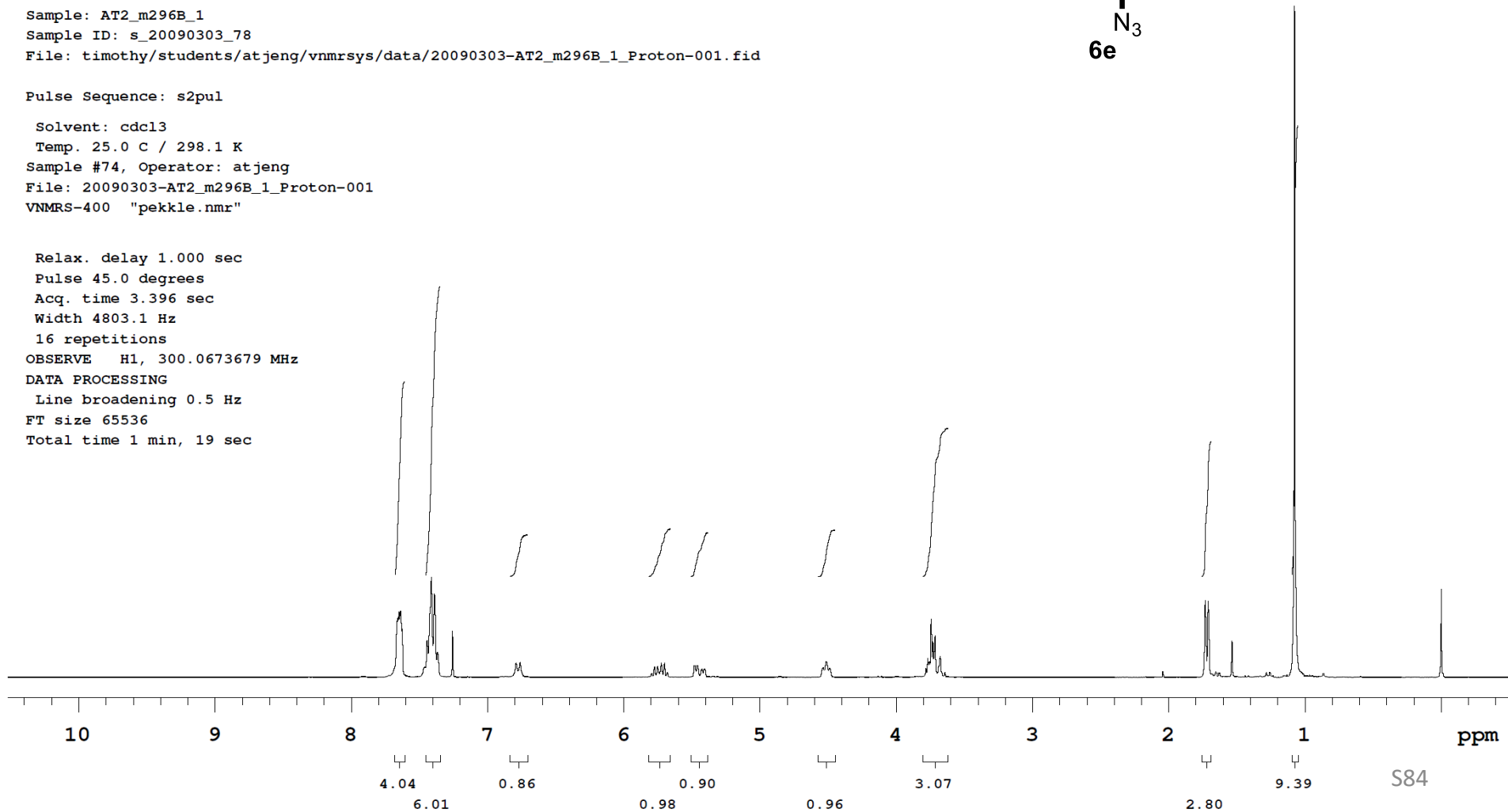


Sample: AT2_m296B_1
Sample ID: s_20090303_78
File: timothy/students/atjeng/vnmrsys/data/20090303-AT2_m296B_1_Proton-001.fid

Pulse Sequence: s2pul

Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Sample #74, Operator: atjeng
File: 20090303-AT2_m296B_1_Proton-001
VNMR-400 "pekkle.nmr"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 3.396 sec
Width 4803.1 Hz
16 repetitions
OBSERVE H1, 300.0673679 MHz
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 1 min, 19 sec



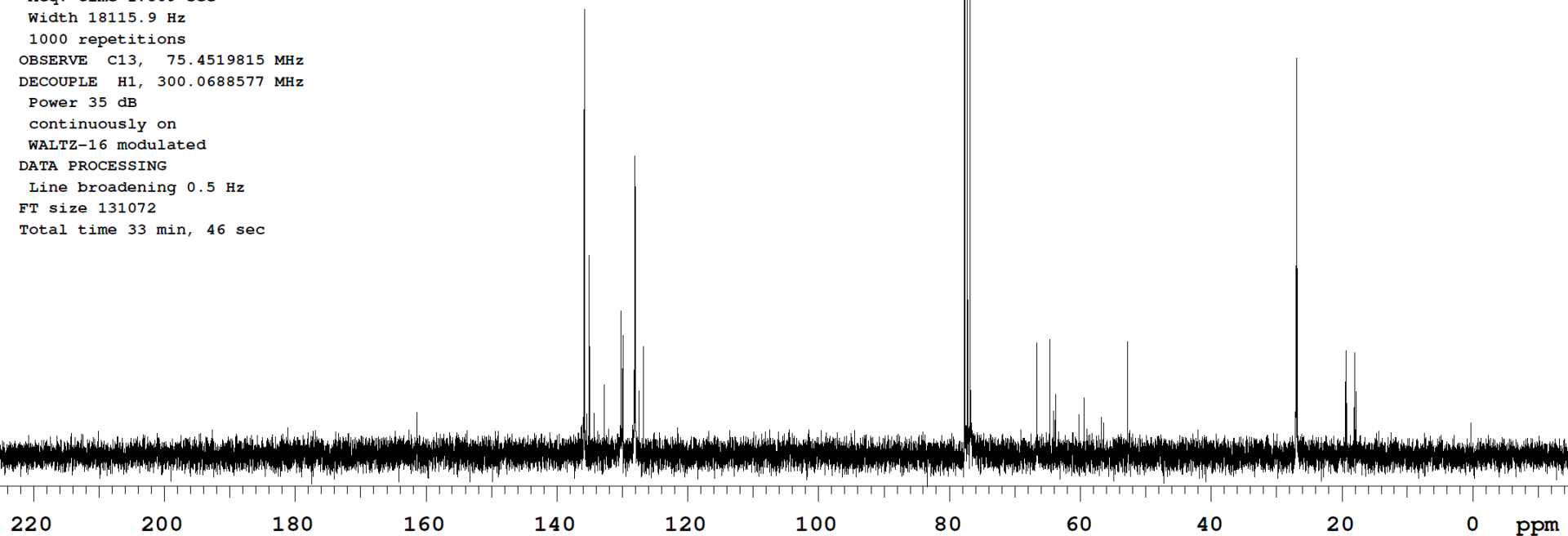
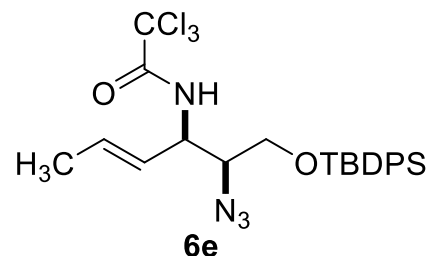
^{13}C NMR of Compound 6e (CDCl_3 ; 75 MHz)

Sample: AT2_m296
Sample ID: s_20110714_06
File: timothy/students/atjeng/vnmrsys/data/20110714-AT2_m296_Carbon-001.fid

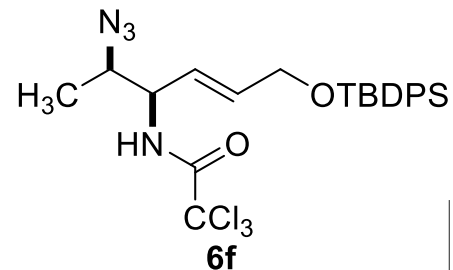
Pulse Sequence: s2pul

Solvent: cdc13
Temp. 25.0 C / 298.1 K
Sample #47, Operator: atjeng
File: 20110714-AT2_m296_Carbon-001
VNMRS-400 "pekkle.nmr"

Relax. delay 0.200 sec
Pulse 45.0 degrees
Acq. time 1.809 sec
Width 18115.9 Hz
1000 repetitions
OBSERVE C13, 75.4519815 MHz
DECOUPLE H1, 300.0688577 MHz
Power 35 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 33 min, 46 sec



^{13}C NMR of Compound 6f (CDCl_3 ; 75 MHz)

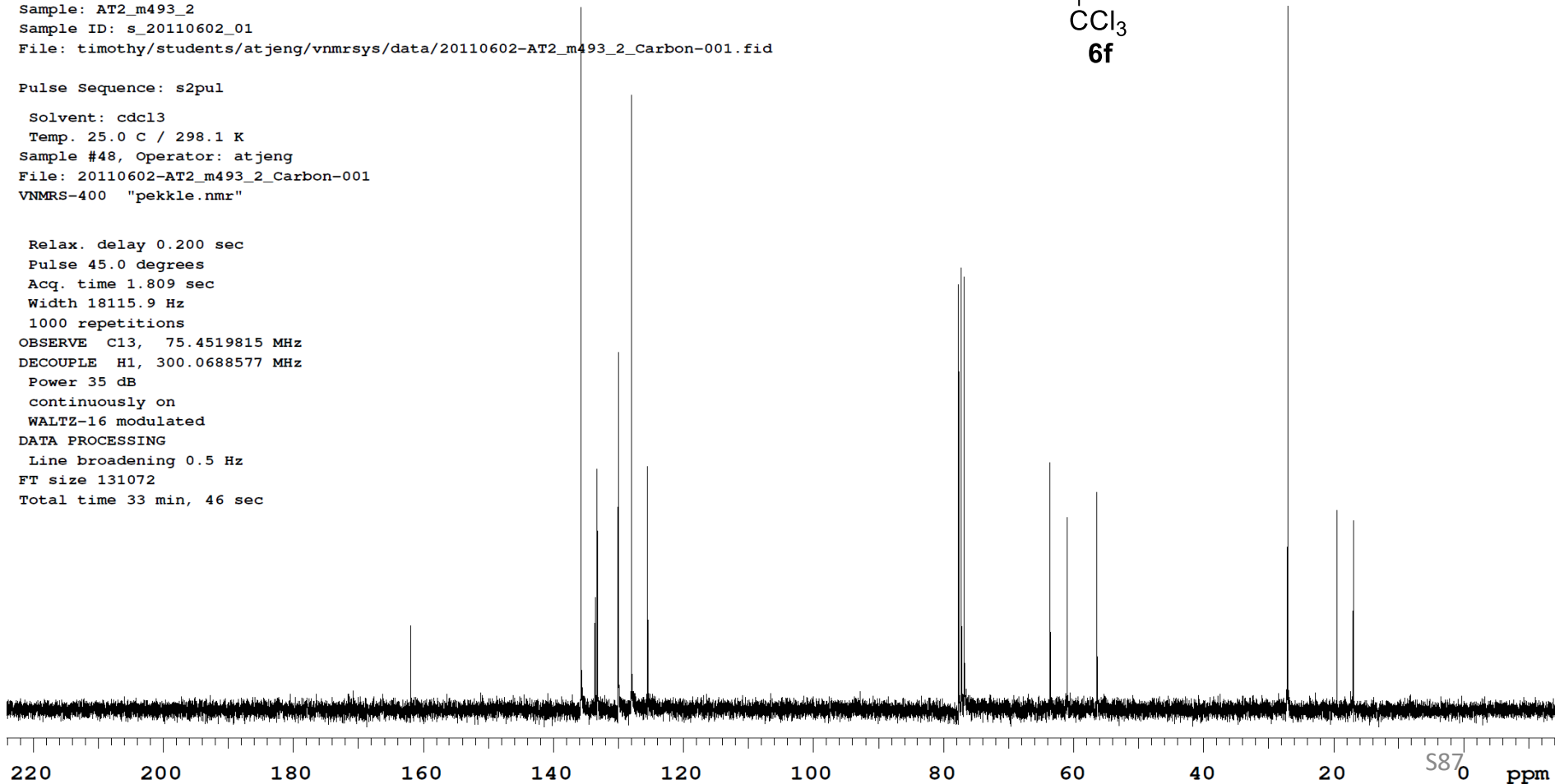


Sample: AT2_m493_2
Sample ID: s_20110602_01
File: timothy/students/atjeng/vnmrsys/data/20110602-AT2_m493_2_Carbon-001.fid

Pulse Sequence: s2pul

Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Sample #48, Operator: atjeng
File: 20110602-AT2_m493_2_Carbon-001
VNMR-400 "pekkle.nmr"

Relax. delay 0.200 sec
Pulse 45.0 degrees
Acq. time 1.809 sec
Width 18115.9 Hz
1000 repetitions
OBSERVE C13, 75.4519815 MHz
DECOUPLE H1, 300.0688577 MHz
Power 35 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 33 min, 46 sec



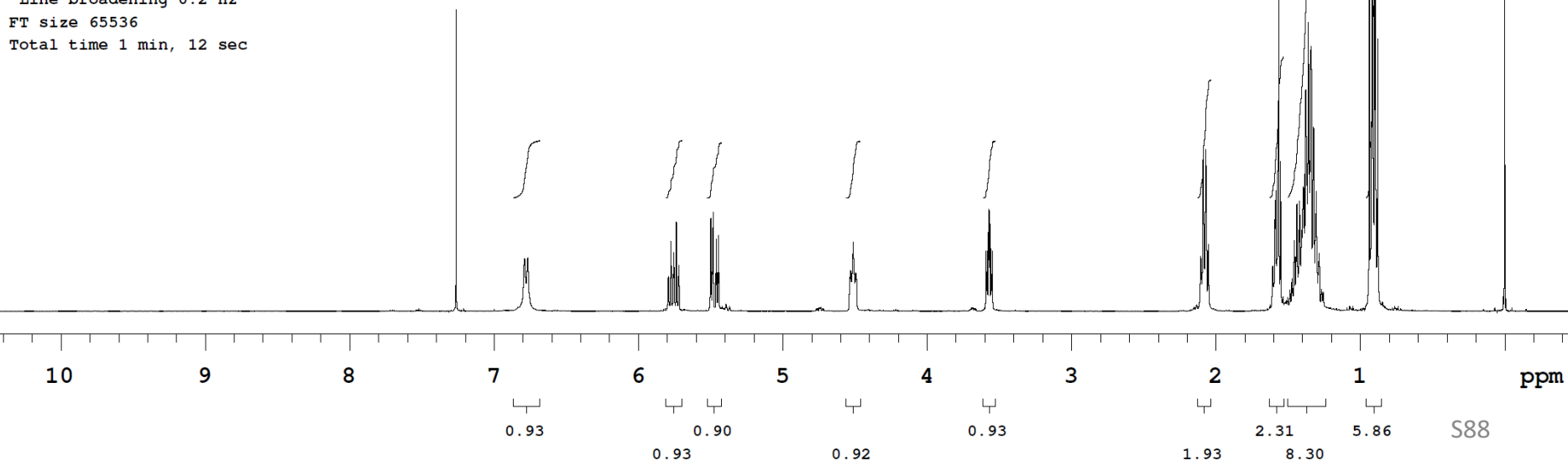
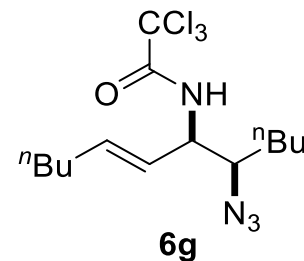
^1H NMR of Compound 6g (CDCl_3 ; 400 MHz)

Sample: AT2_m497_2
Sample ID: s_20110703_03
File: timothy/students/atjeng/vnmrsys/data/20110703-AT2_m497_2_Proton-002.fid

Pulse Sequence: s2pul

Solvent: cdcl_3
Temp. 25.0 C / 298.1 K
Sample #75, Operator: atjeng
File: 20110703-AT2_m497_2_Proton-002
VNMR-400 "pekkle.nmr"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.992 sec
Width 6385.7 Hz
16 repetitions
OBSERVE H1, 399.3851851 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 12 sec



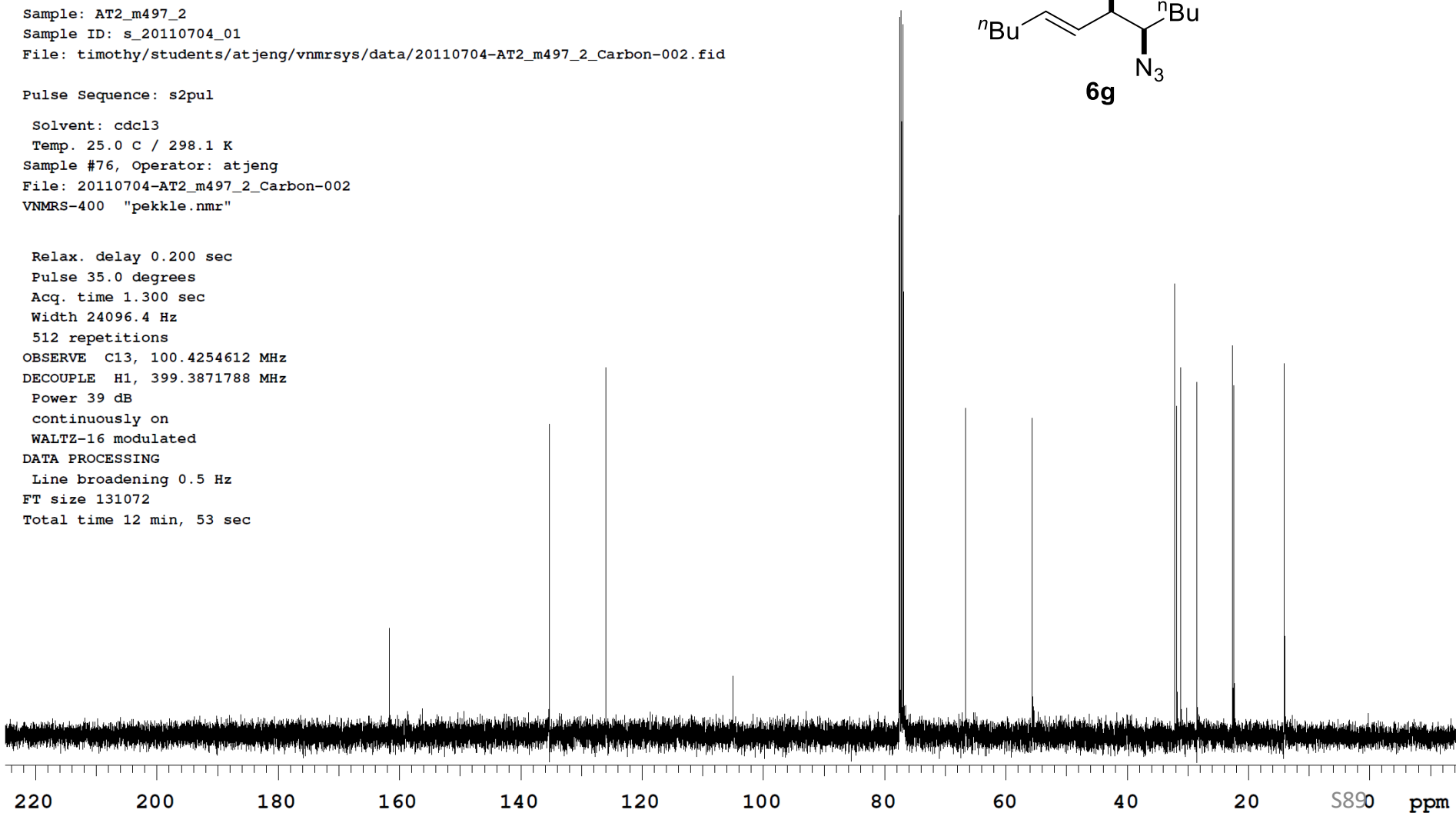
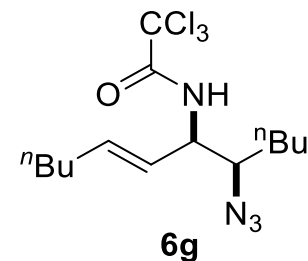
^{13}C NMR of Compound 6g (CDCl_3 ; 100 MHz)

Sample: AT2_m497_2
Sample ID: s_20110704_01
File: timothy/students/atjeng/vnmrsys/data/20110704-AT2_m497_2_Carbon-002.fid

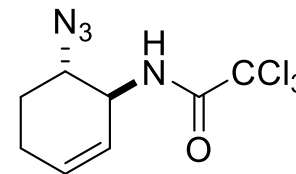
Pulse Sequence: s2pul

Solvent: cdcl_3
Temp. 25.0 C / 298.1 K
Sample #76, Operator: atjeng
File: 20110704-AT2_m497_2_Carbon-002
VNMRS-400 "pekkle.nmr"

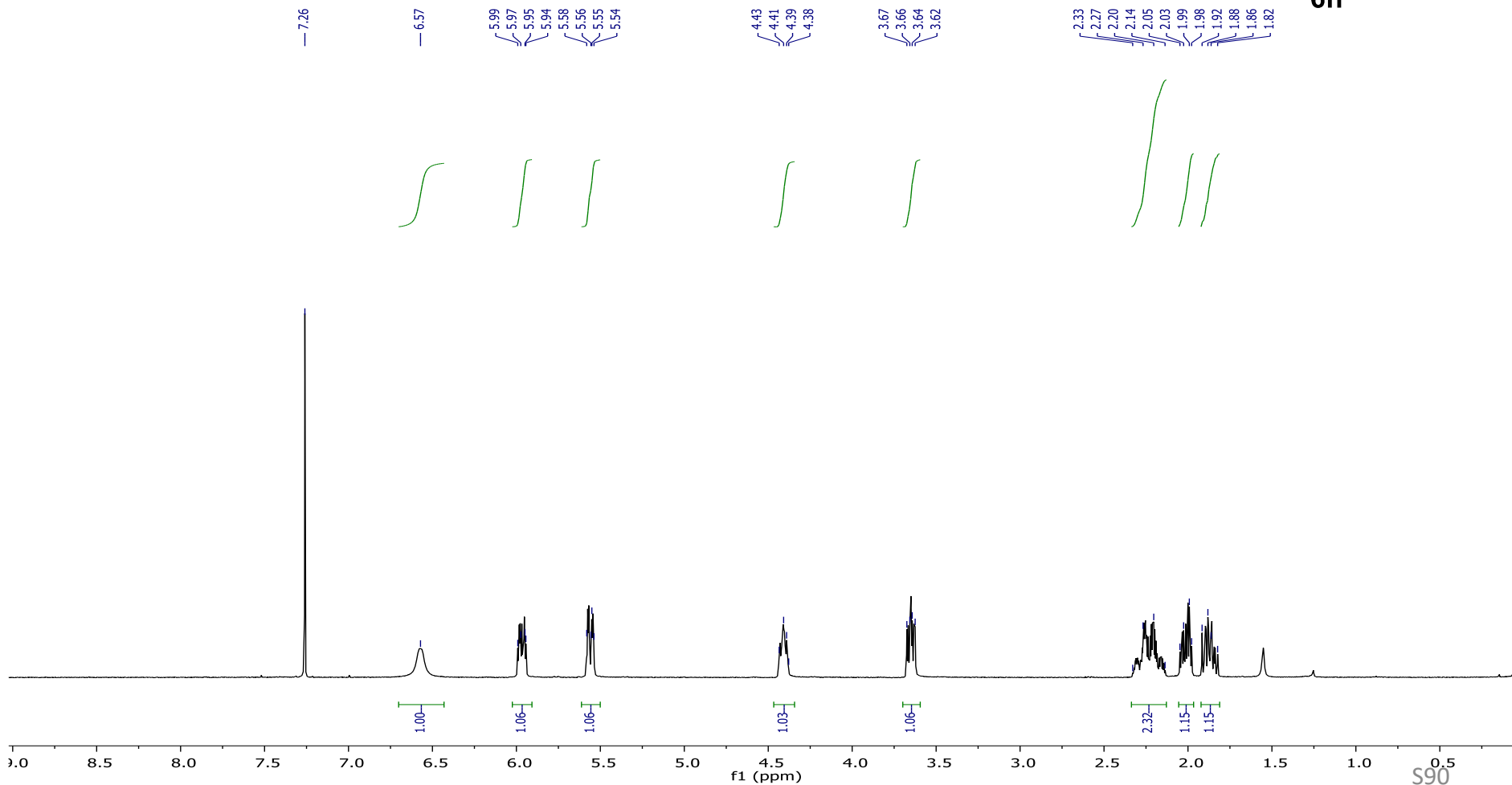
Relax. delay 0.200 sec
Pulse 35.0 degrees
Acq. time 1.300 sec
Width 24096.4 Hz
512 repetitions
OBSERVE C13, 100.4254612 MHz
DECOUPLE H1, 399.3871788 MHz
Power 39 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 12 min, 53 sec



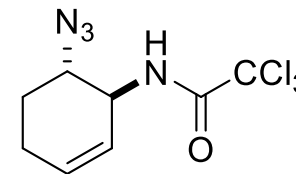
^1H NMR of Compound 6h (CDCl_3 ; 400 MHz)



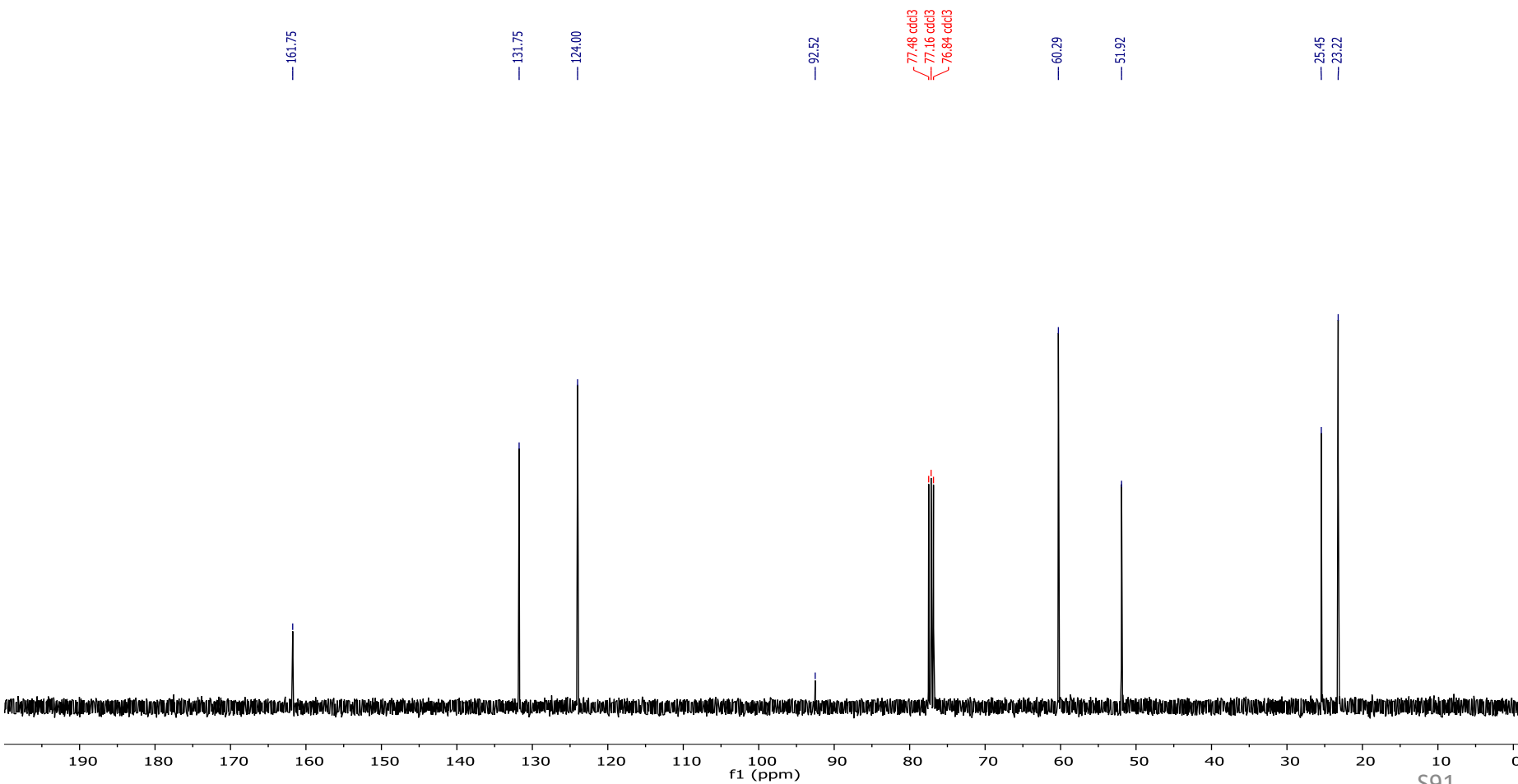
6h



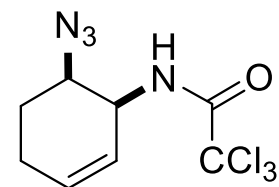
^{13}C NMR of Compound 6h (CDCl_3 ; 100 MHz)



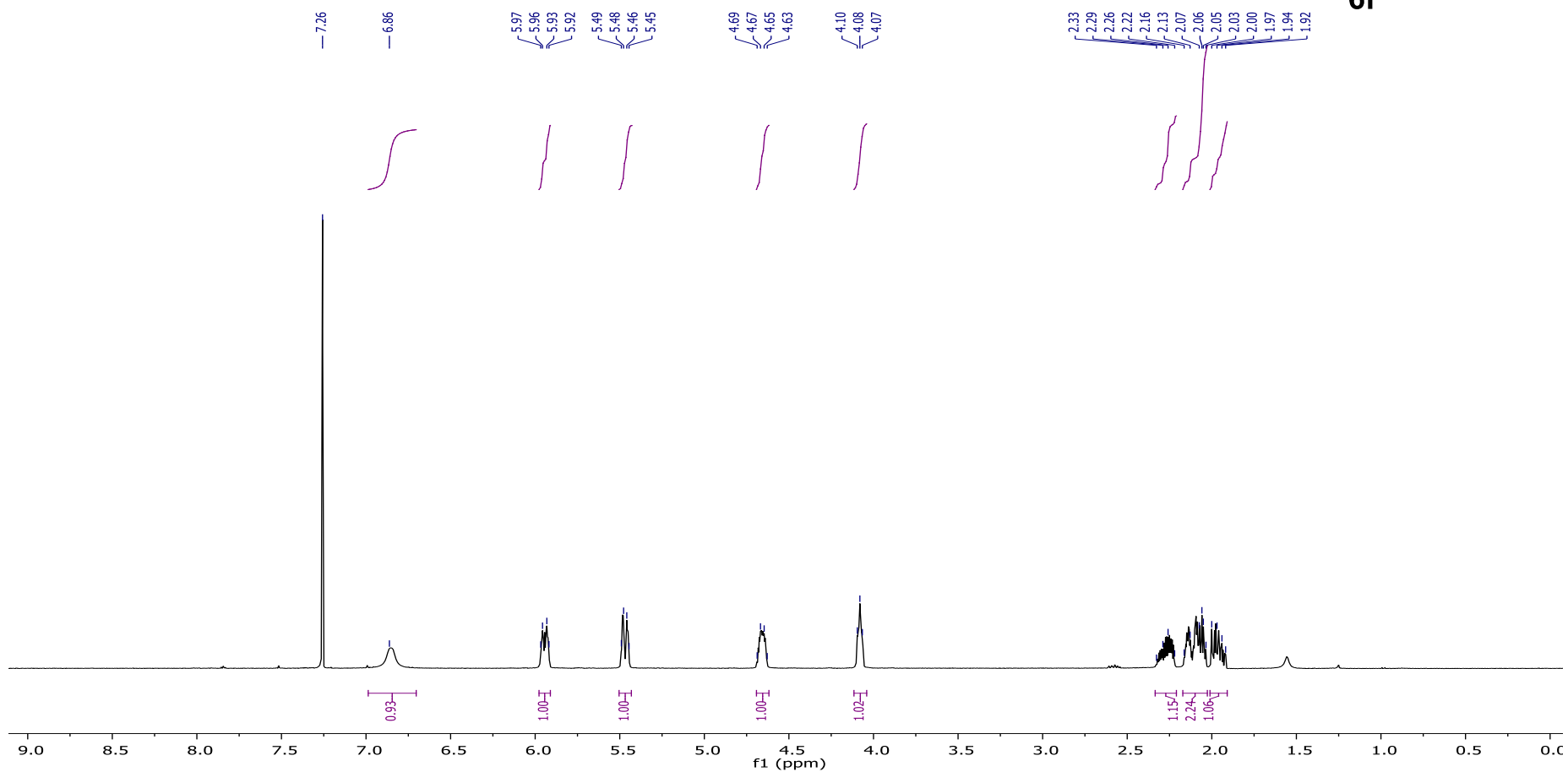
6h



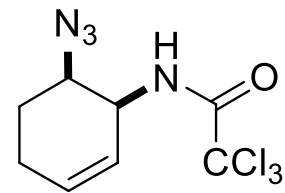
¹H NMR of Compound 6i (CDCl₃; 400 MHz)



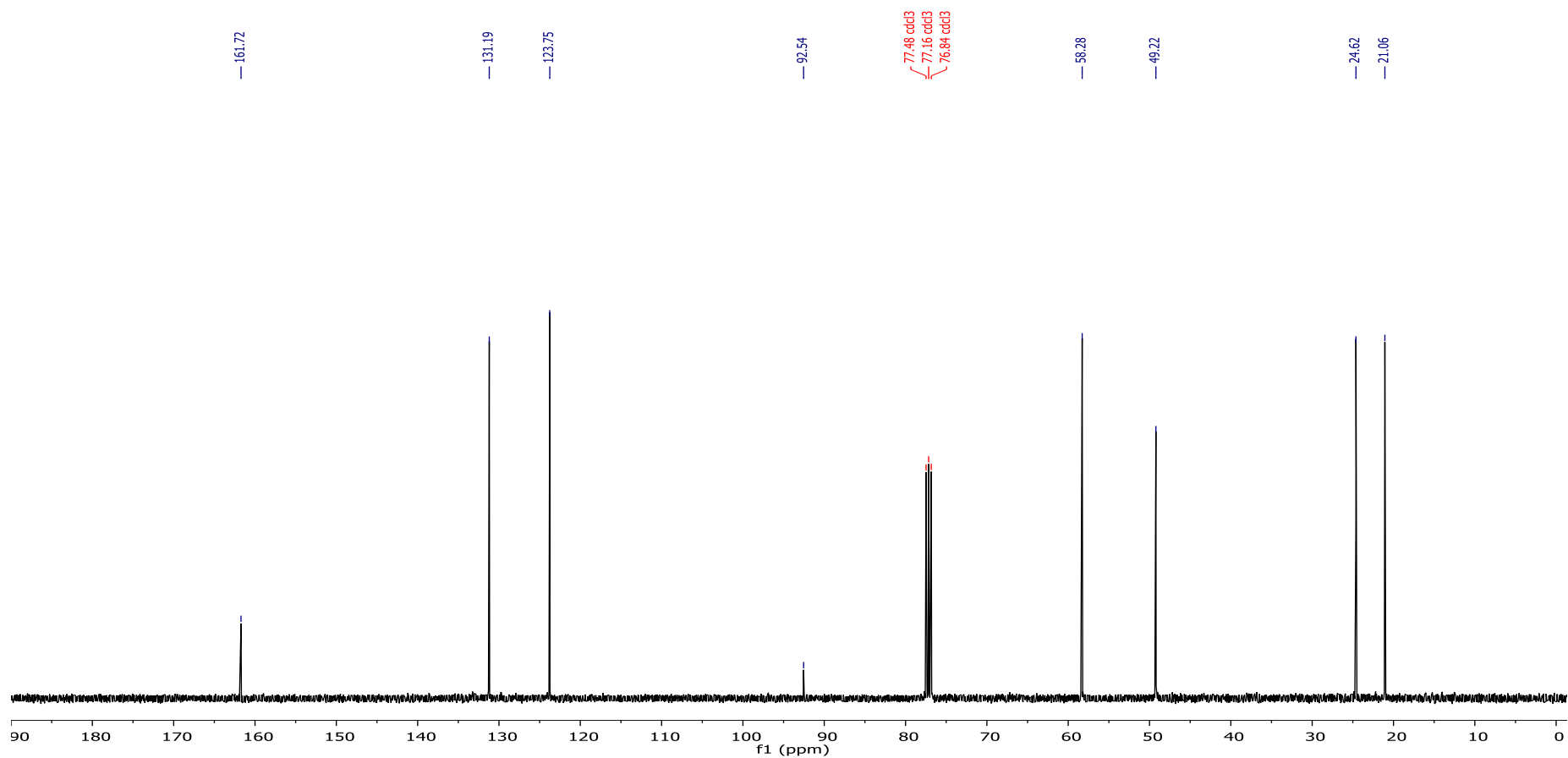
6i



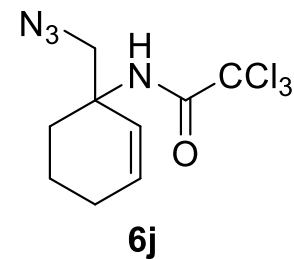
^{13}C NMR of Compound 6i (CDCl_3 ; 100 MHz)



6i



^1H NMR of Compound 6j (CDCl_3 ; 400 MHz)

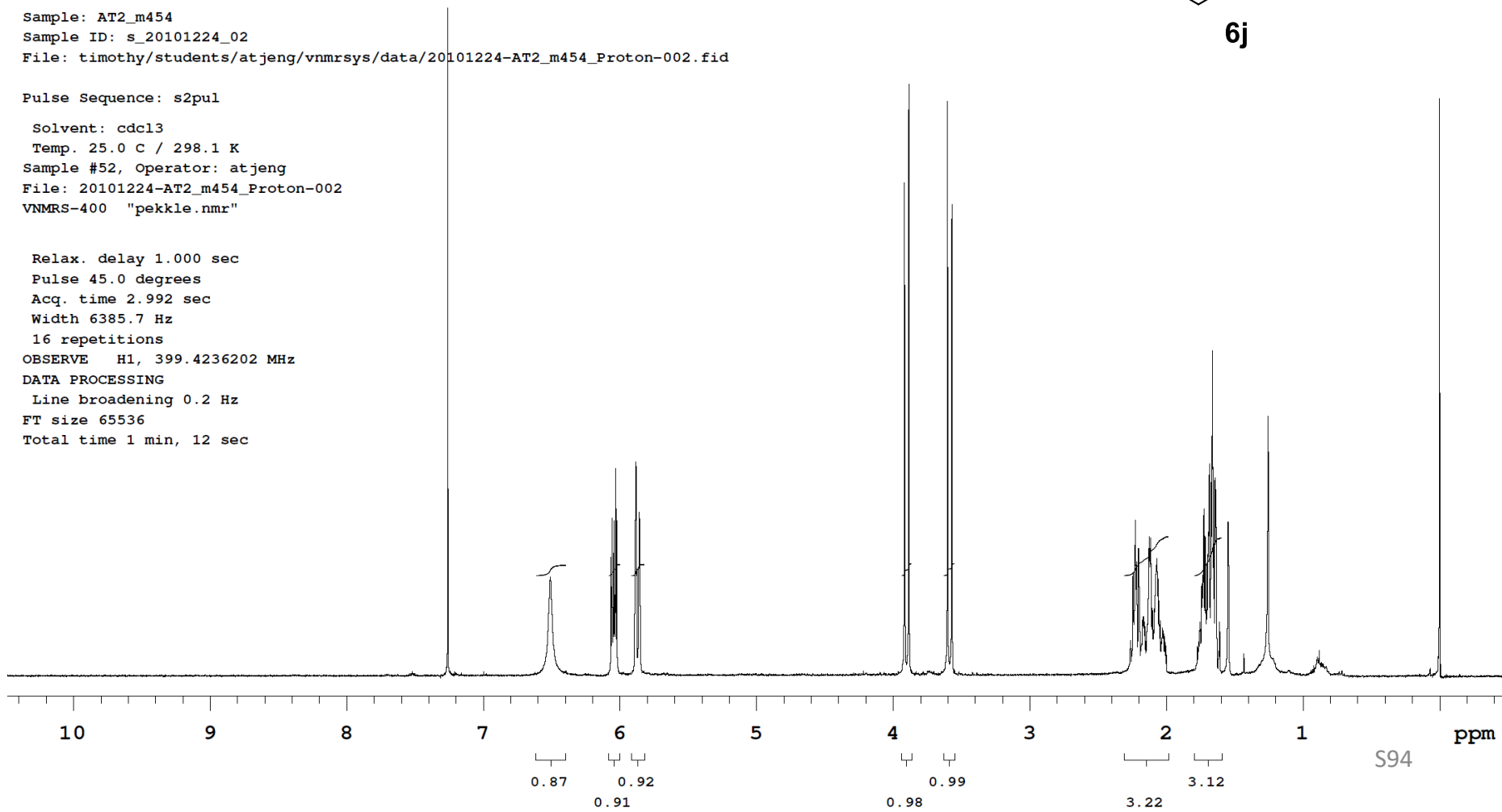


Sample: AT2_m454
Sample ID: s_20101224_02
File: timothy/students/atjeng/vnmrsys/data/20101224-AT2_m454_Proton-002.fid

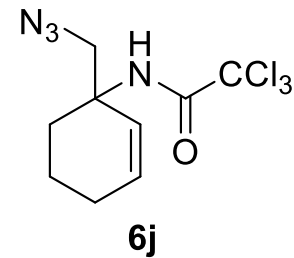
Pulse Sequence: s2pul

Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Sample #52, Operator: atjeng
File: 20101224-AT2_m454_Proton-002
VNMR-400 "pekkle.nmr"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.992 sec
Width 6385.7 Hz
16 repetitions
OBSERVE H1, 399.4236202 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 12 sec



^{13}C NMR of Compound 6j (CDCl_3 ; 100 MHz)

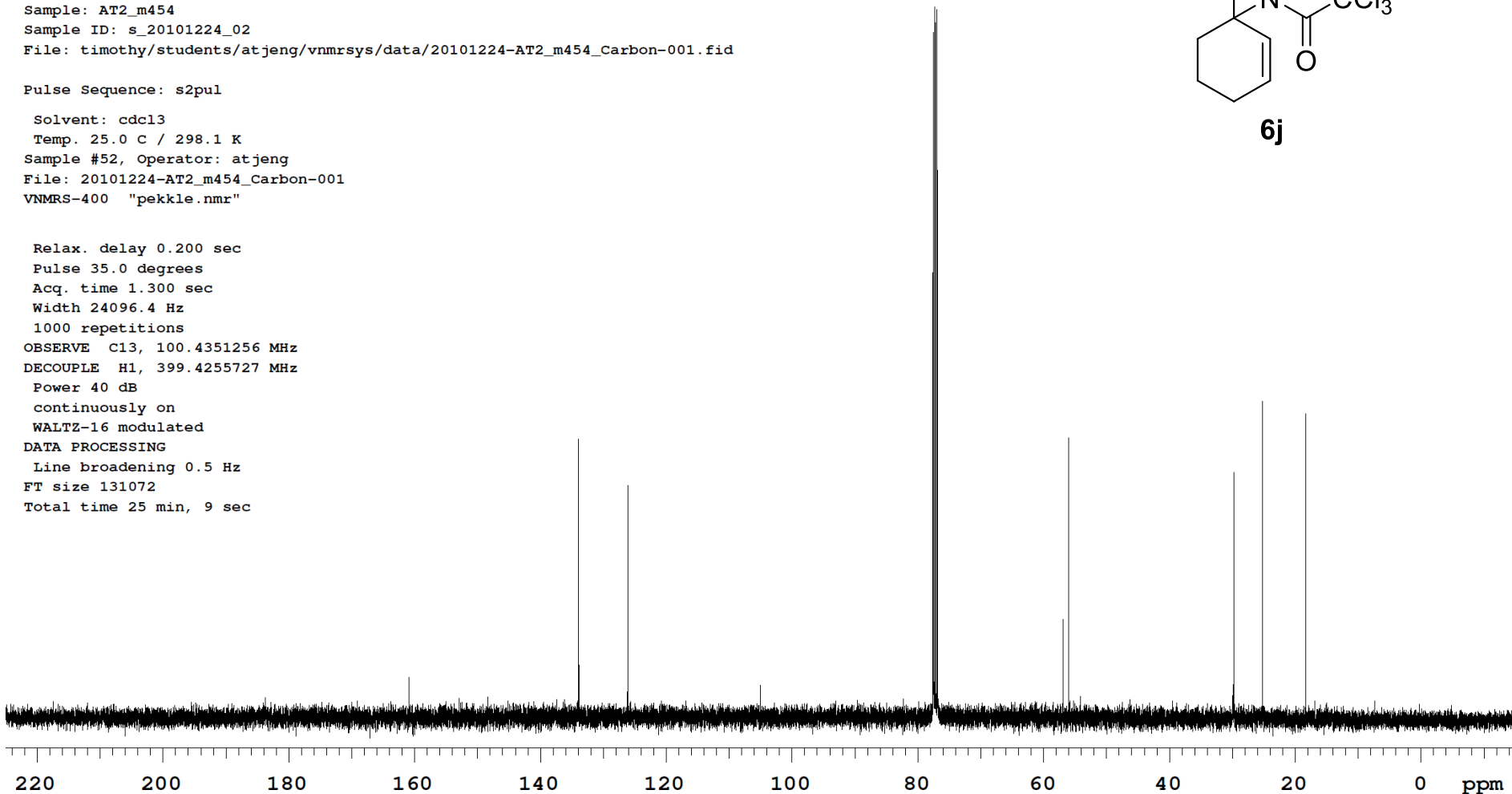


Sample: AT2_m454
Sample ID: s_20101224_02
File: timothy/students/atjeng/vnmrsys/data/20101224-AT2_m454_Carbon-001.fid

Pulse Sequence: s2pul

Solvent: cdc13
Temp. 25.0 C / 298.1 K
Sample #52, Operator: atjeng
File: 20101224-AT2_m454_Carbon-001
VNMRS-400 "pekkle.nmr"

Relax. delay 0.200 sec
Pulse 35.0 degrees
Acq. time 1.300 sec
Width 24096.4 Hz
1000 repetitions
OBSERVE C13, 100.4351256 MHz
DECOUPLE H1, 399.4255727 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 25 min, 9 sec



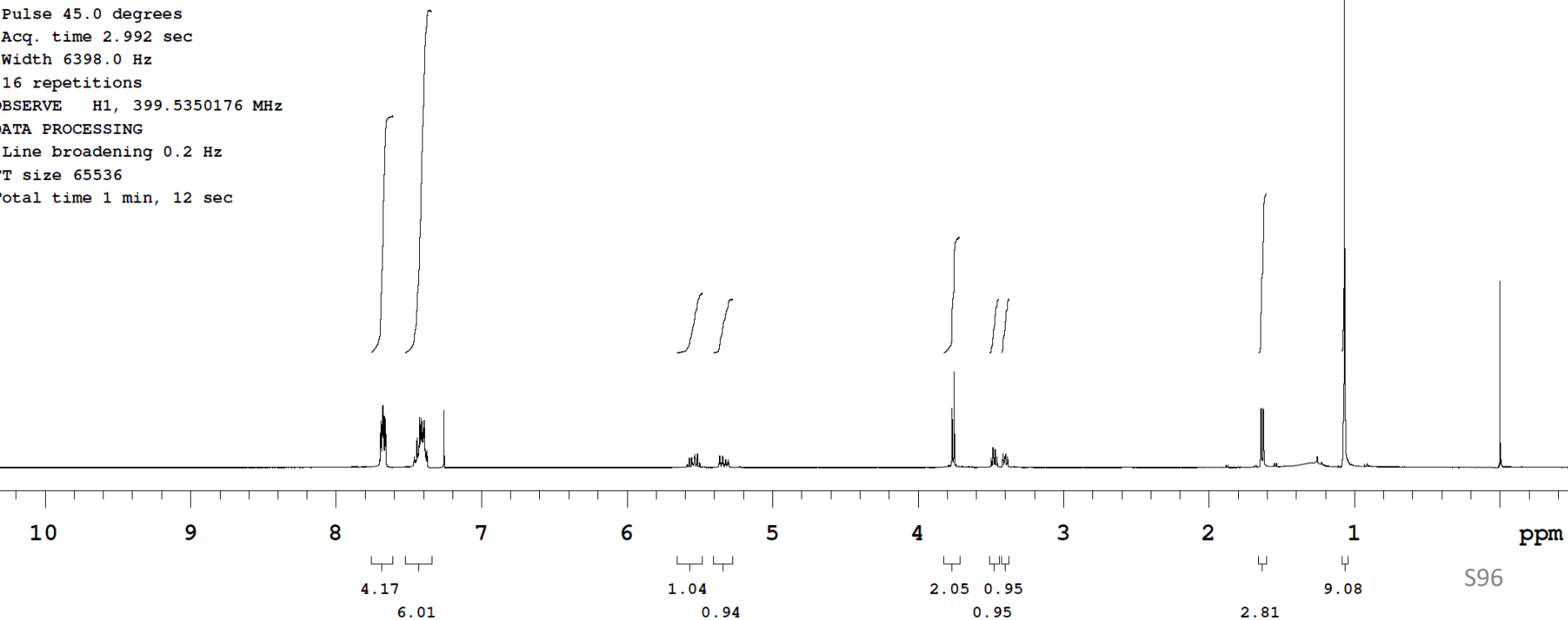
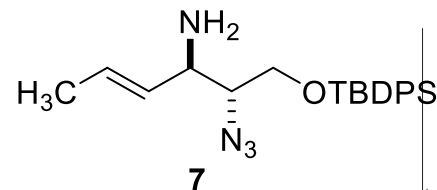
^1H NMR of Compound 7 (CDCl_3 ; 400 MHz)

Sample: AT4_313C_1
Sample ID: s_20090618_39
File: timothy/students/atjeng/vnmrsys/data/20090618-AT4_313C_1_PROTON-002.fid

Pulse Sequence: s2pul

Solvent: cdcl_3
Temp. 25.0 C / 298.1 K
Sample #36, Operator: atjeng
File: 20090618-AT4_313C_1_PROTON-002
NMRS-400 "pekkle.nmr"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.992 sec
Width 6398.0 Hz
16 repetitions
OBSERVE H1, 399.5350176 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 12 sec



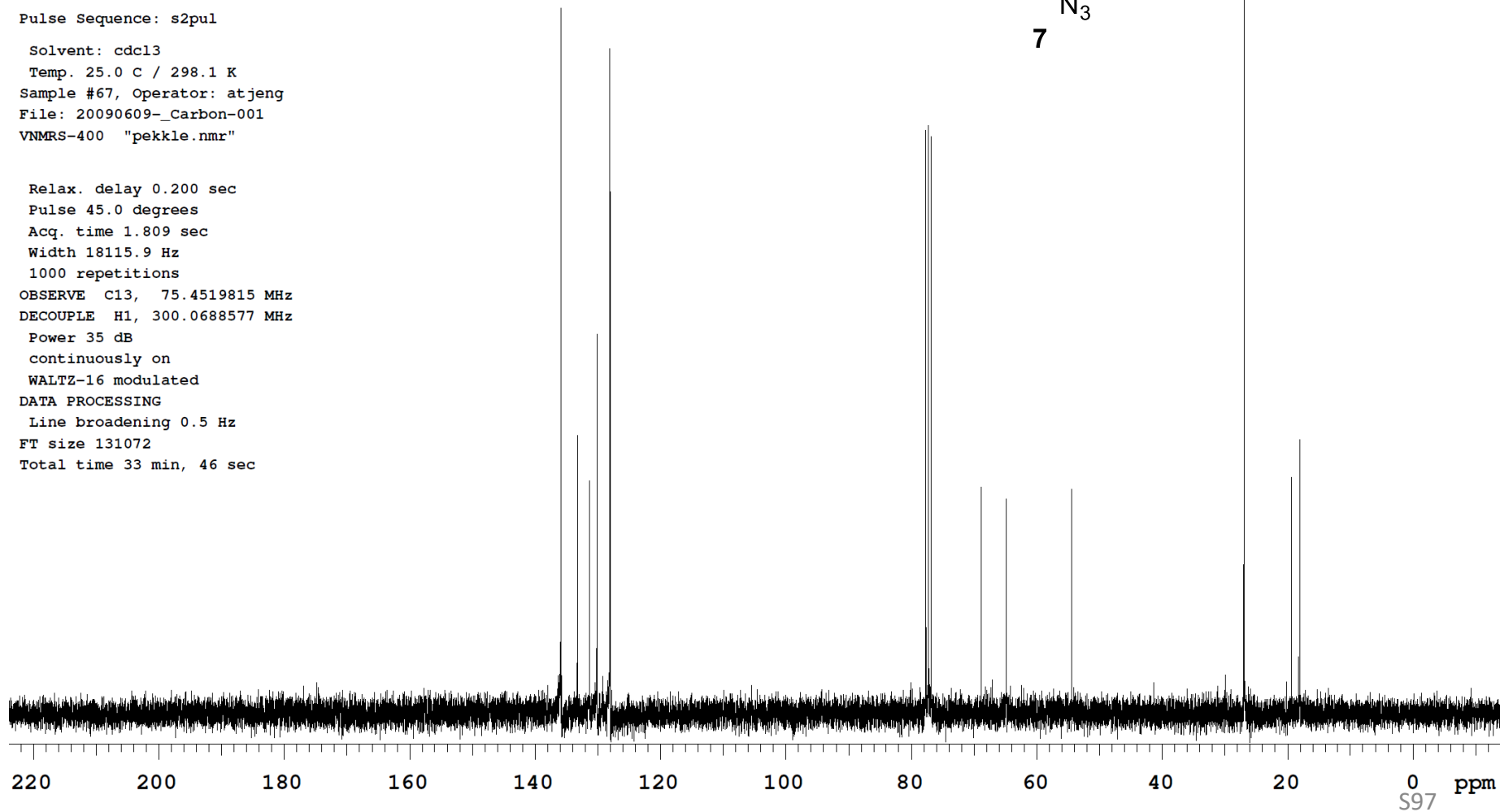
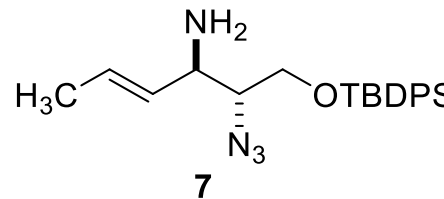
^{13}C NMR of Compound 7 (CDCl_3 ; 75 MHz)

Sample ID: s_20090609_67
File: timothy/students/atjeng/vnmrsys/data/20090609-_Carbon-001.fid

Pulse Sequence: s2pul

Solvent: cdcl_3
Temp. 25.0 C / 298.1 K
Sample #67, Operator: atjeng
File: 20090609-_Carbon-001
VNMR-400 "pekkle.nmr"

Relax. delay 0.200 sec
Pulse 45.0 degrees
Acq. time 1.809 sec
Width 18115.9 Hz
1000 repetitions
OBSERVE C13, 75.4519815 MHz
DECOUPLE H1, 300.0688577 MHz
Power 35 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 33 min, 46 sec

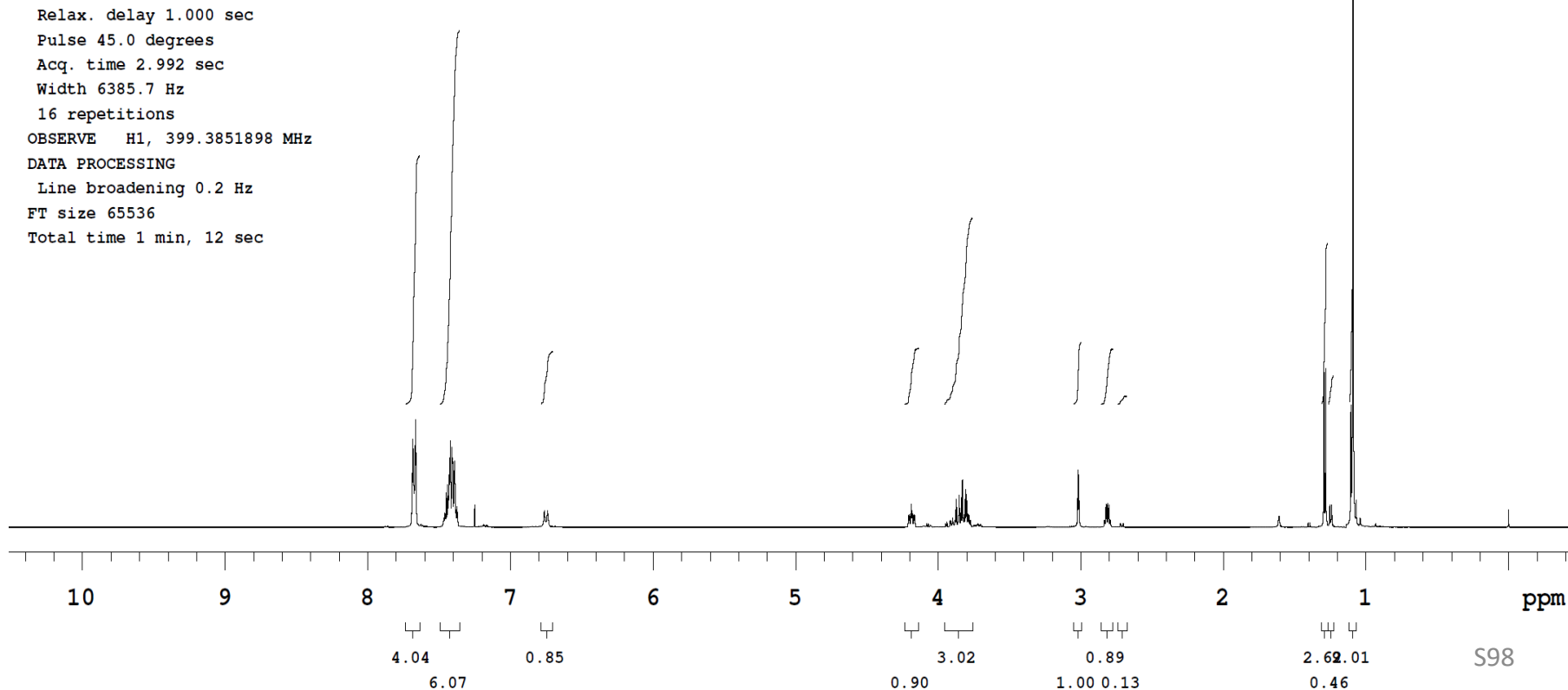
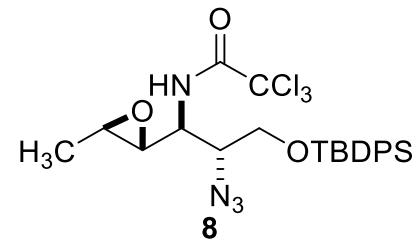


^1H NMR of Compound 8 (CDCl_3 ; 400 MHz)

Sample: AT4_311_1
Sample ID: s_20110612_03
File: timothy/students/atjeng/vnmrsys/data/20110612-AT4_311_1_Proton-002.fid

Pulse Sequence: s2pul

Solvent: cdcl_3
Temp. 25.0 C / 298.1 K
Sample #37, Operator: atjeng
File: 20110612-AT4_311_1_Proton-002
VNMR-400 "pekkle.nmr"



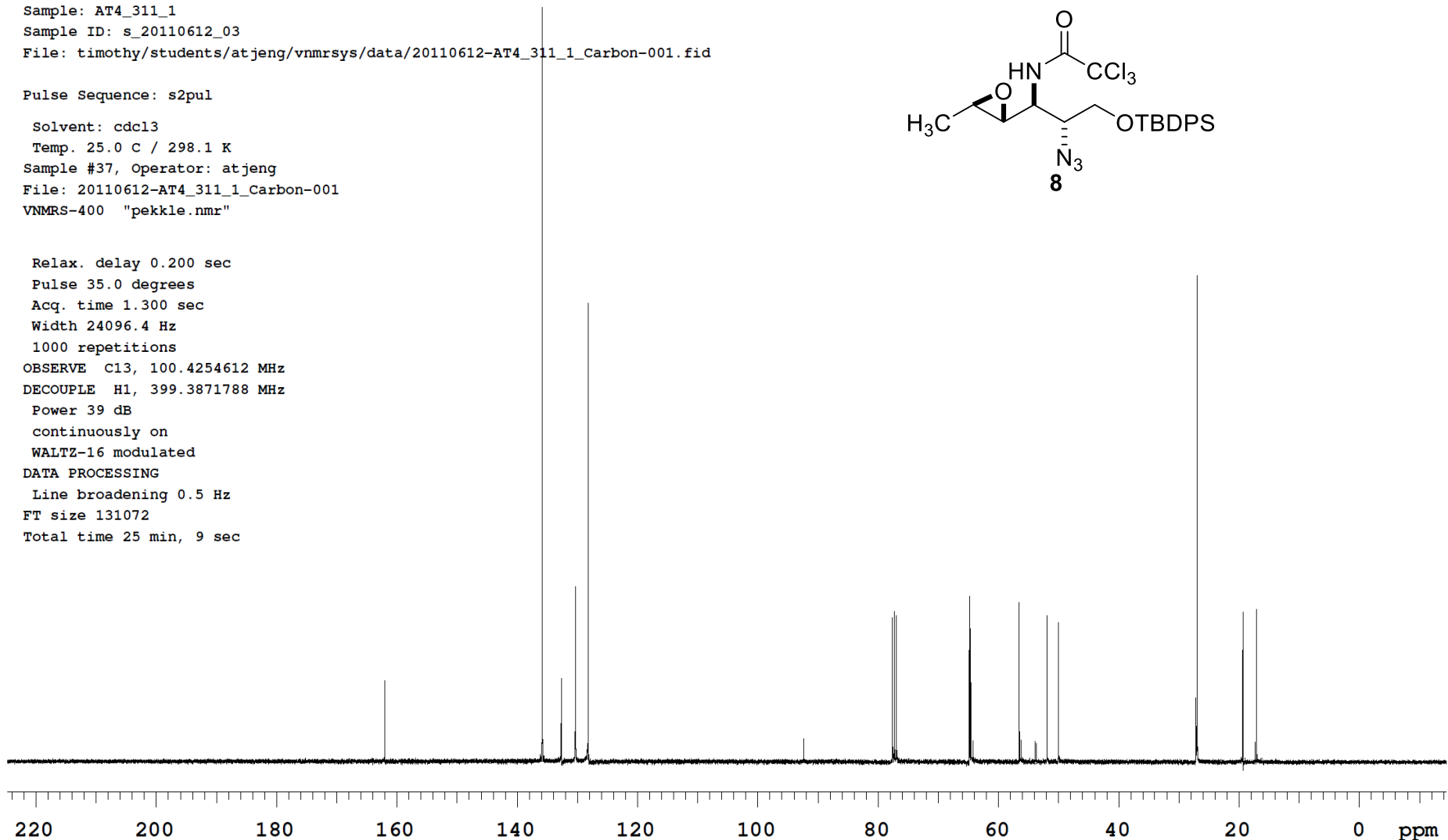
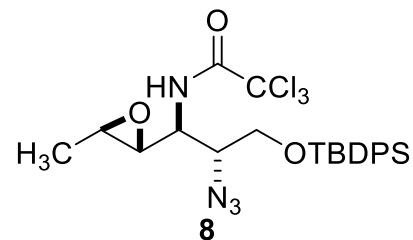
^{13}C NMR of Compound 8 (CDCl_3 ; 100 MHz)

Sample: AT4_311_1
Sample ID: s_20110612_03
File: timothy/students/atjeng/vnmrsys/data/20110612-AT4_311_1_Carbon-001.fid

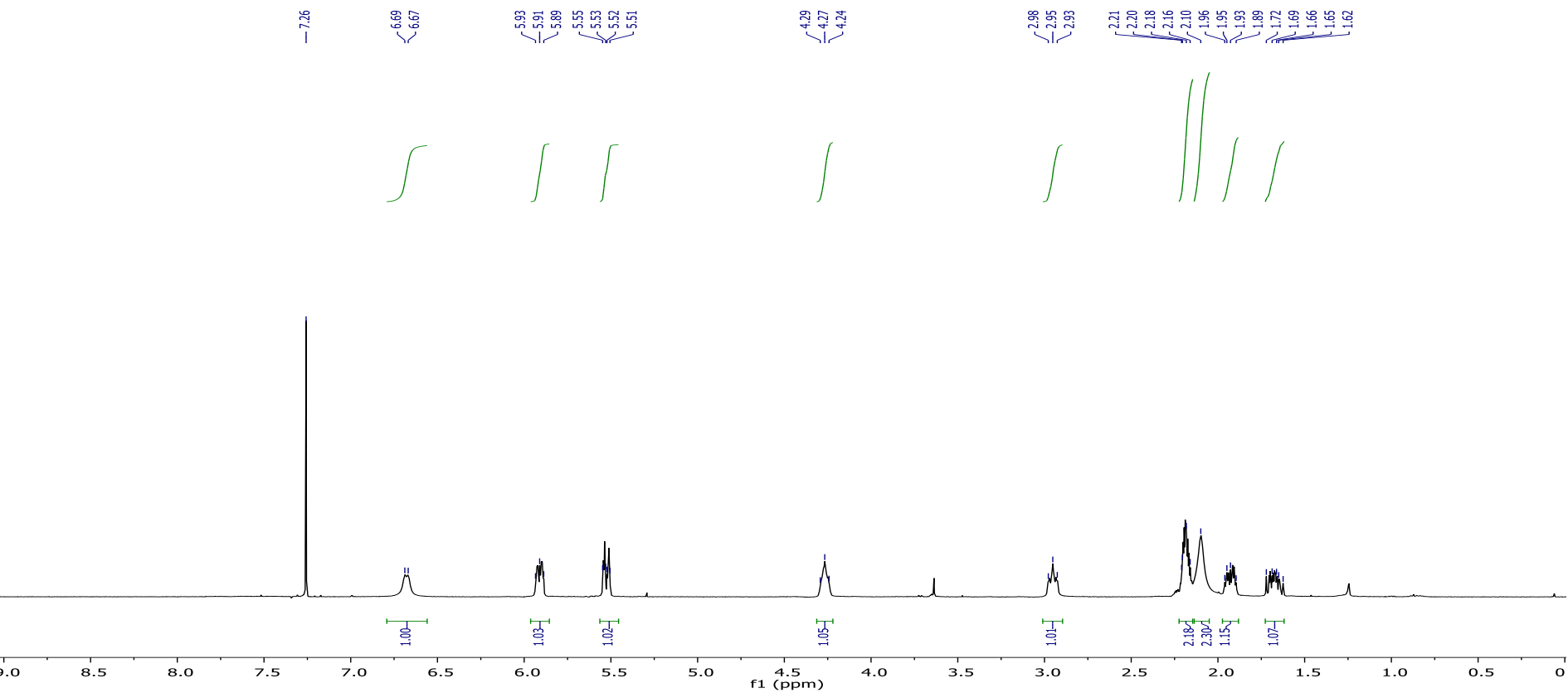
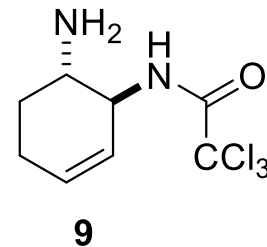
Pulse Sequence: s2pul

Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Sample #37, Operator: atjeng
File: 20110612-AT4_311_1_Carbon-001
VNMR-400 "pekkle.nmr"

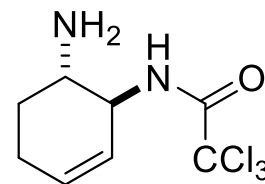
Relax. delay 0.200 sec
Pulse 35.0 degrees
Acq. time 1.300 sec
Width 24096.4 Hz
1000 repetitions
OBSERVE C13, 100.4254612 MHz
DECOUPLE H1, 399.3871788 MHz
Power 39 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 25 min, 9 sec



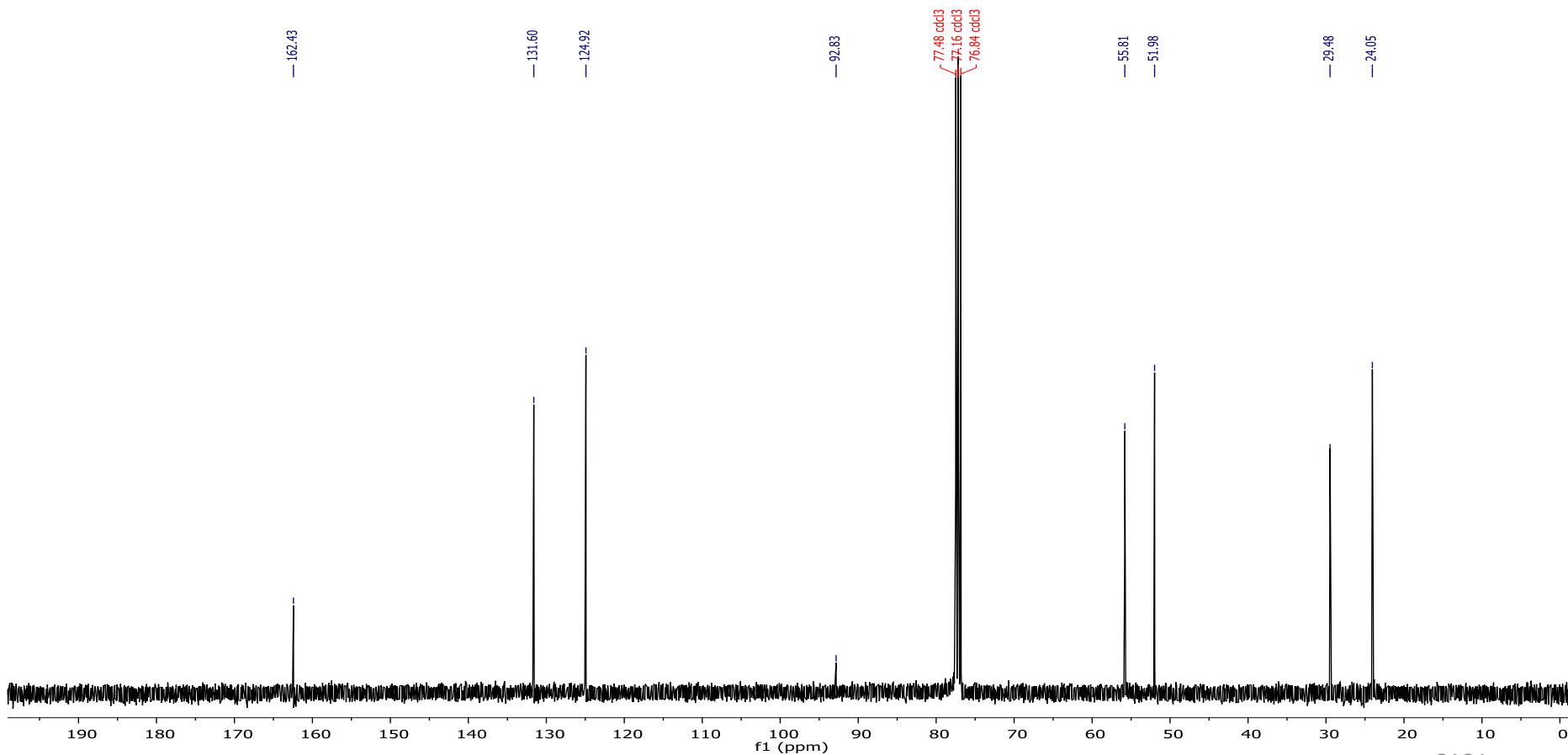
^1H NMR of Compound 9 (CDCl_3 ; 400 MHz)



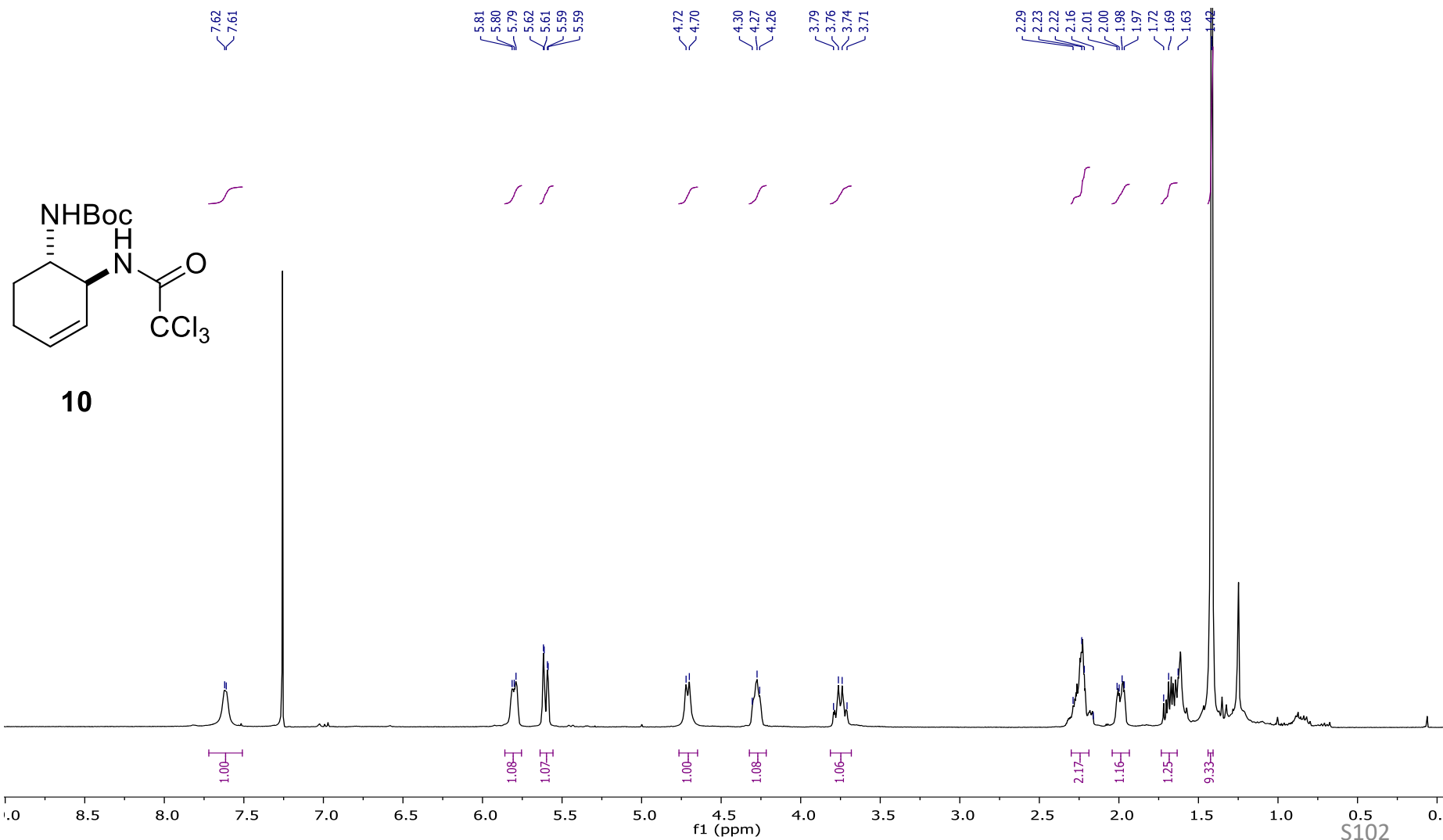
^{13}C NMR of Compound 9 (CDCl_3 ; 100 MHz)



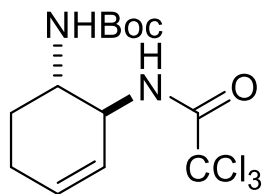
9



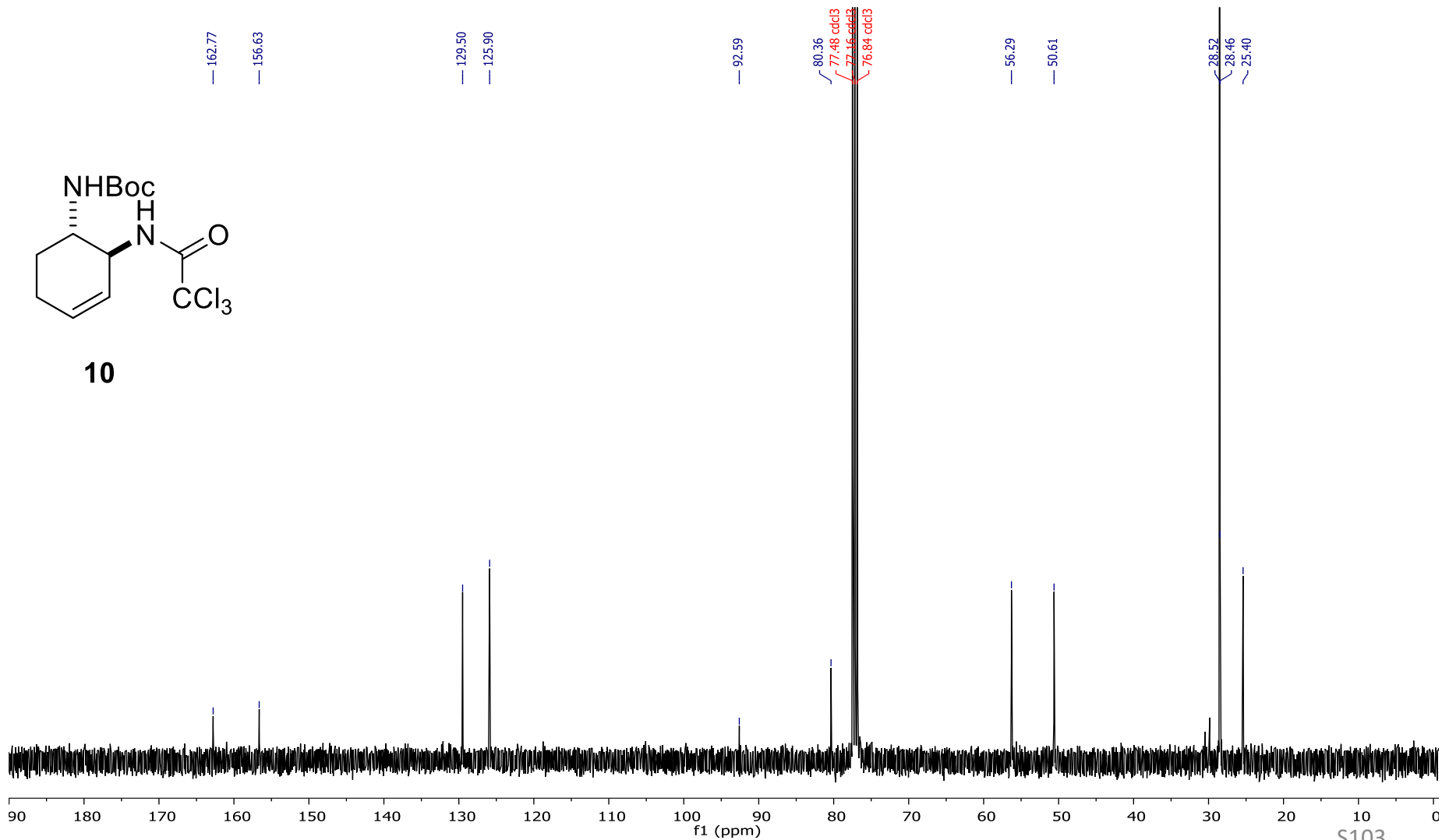
^1H NMR of Compound 10 (CDCl_3 ; 400 MHz)



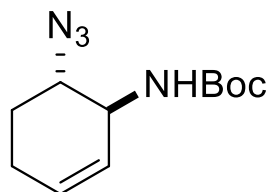
^{13}C NMR of Compound 10 (CDCl_3 ; 100 MHz)



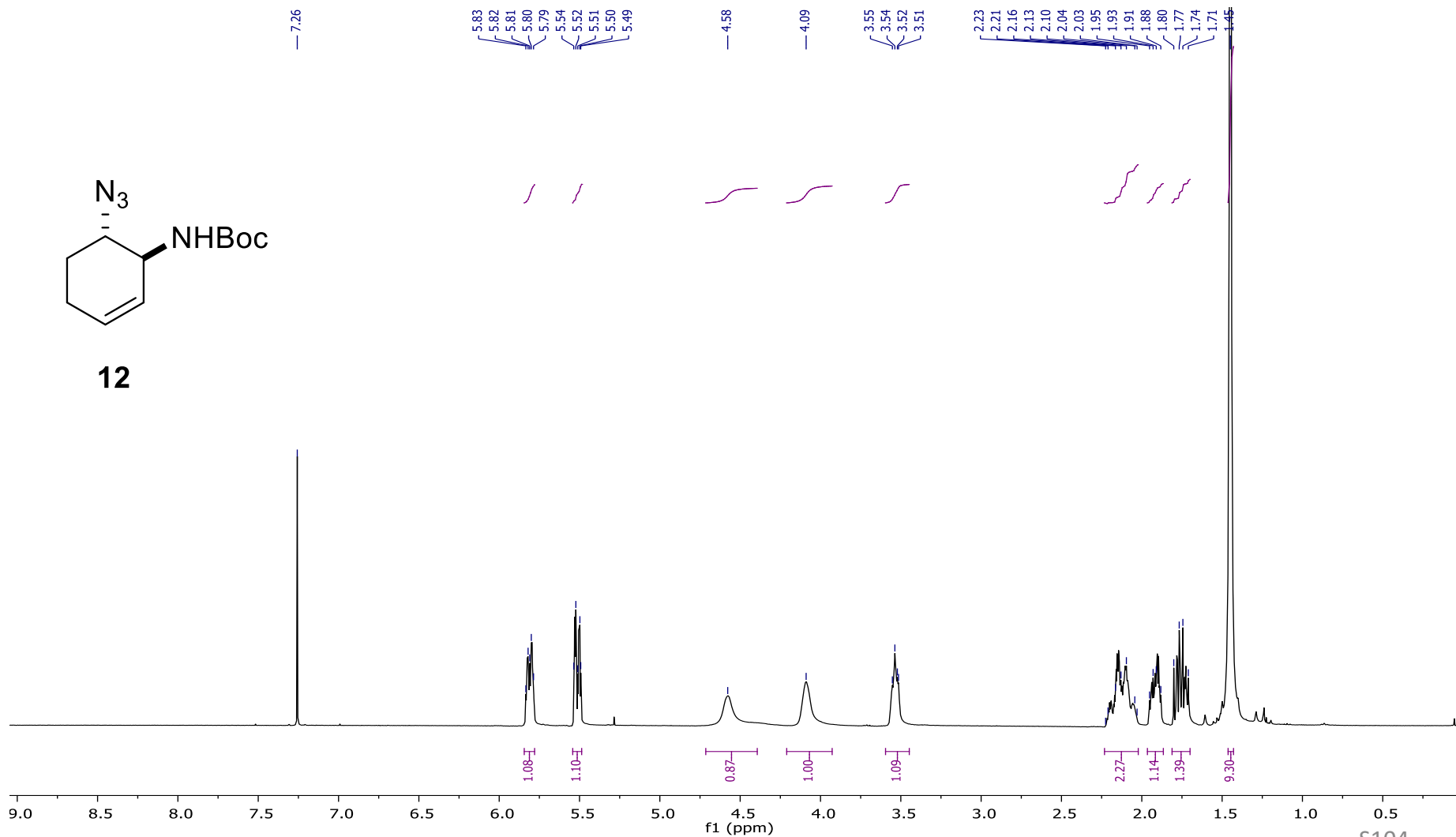
10



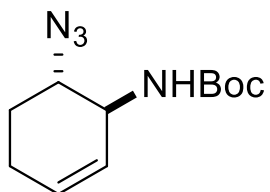
^1H NMR of Compound 12 (CDCl_3 ; 400 MHz)



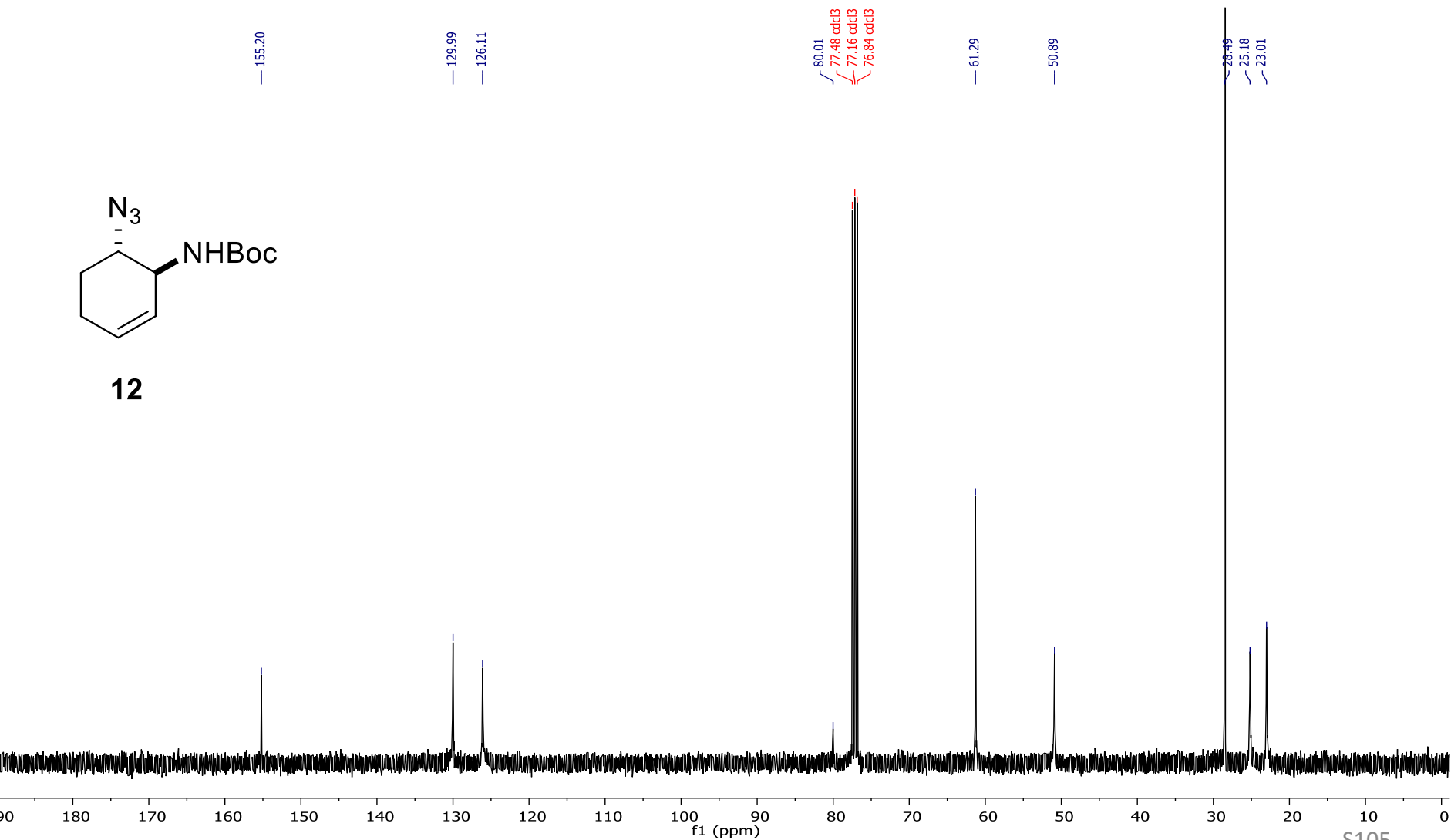
12



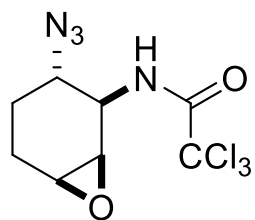
^{13}C NMR of Compound 12 (CDCl_3 ; 100 MHz)



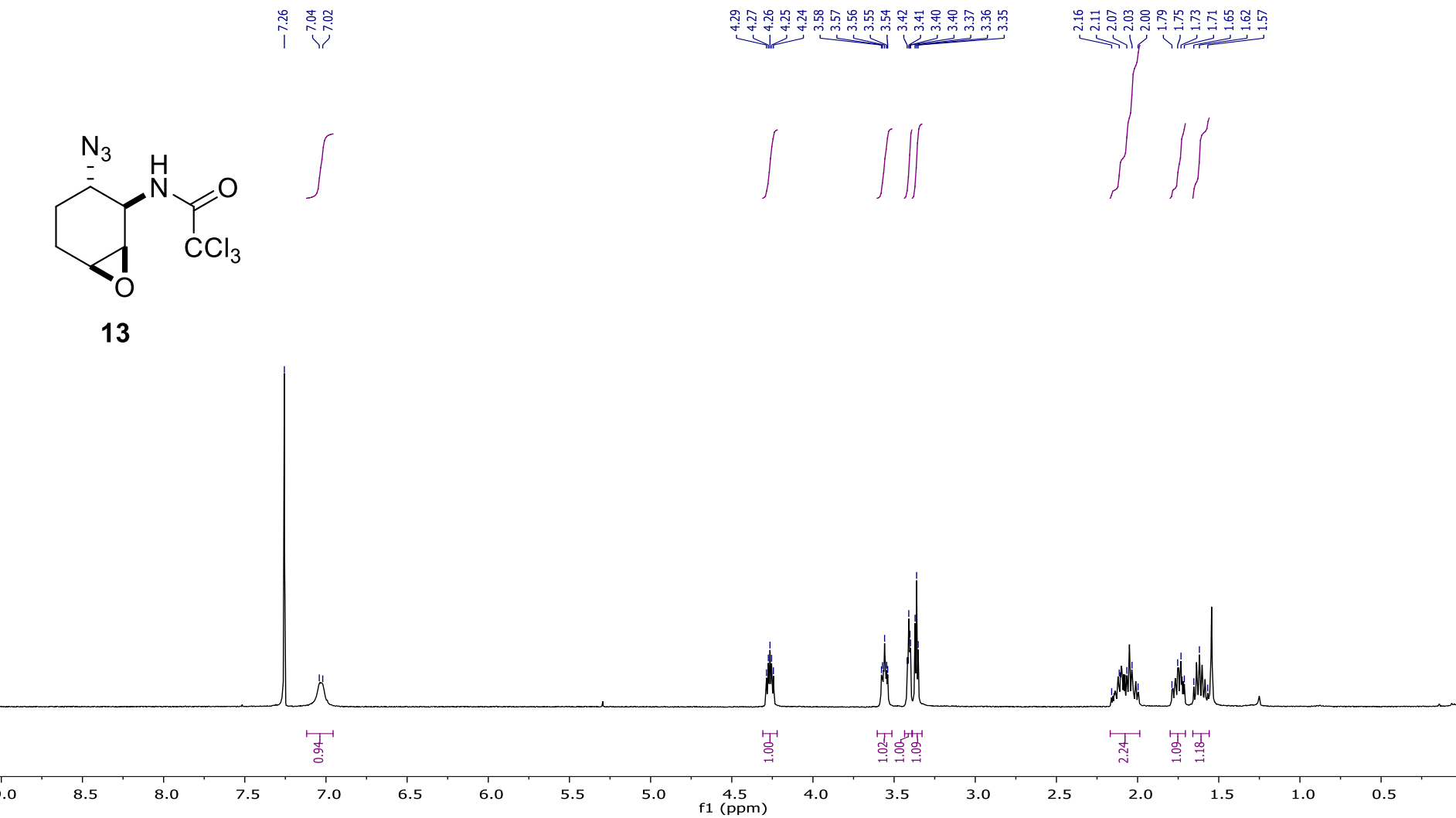
12



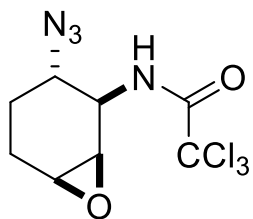
^1H NMR of Compound 13 (CDCl_3 ; 400 MHz)



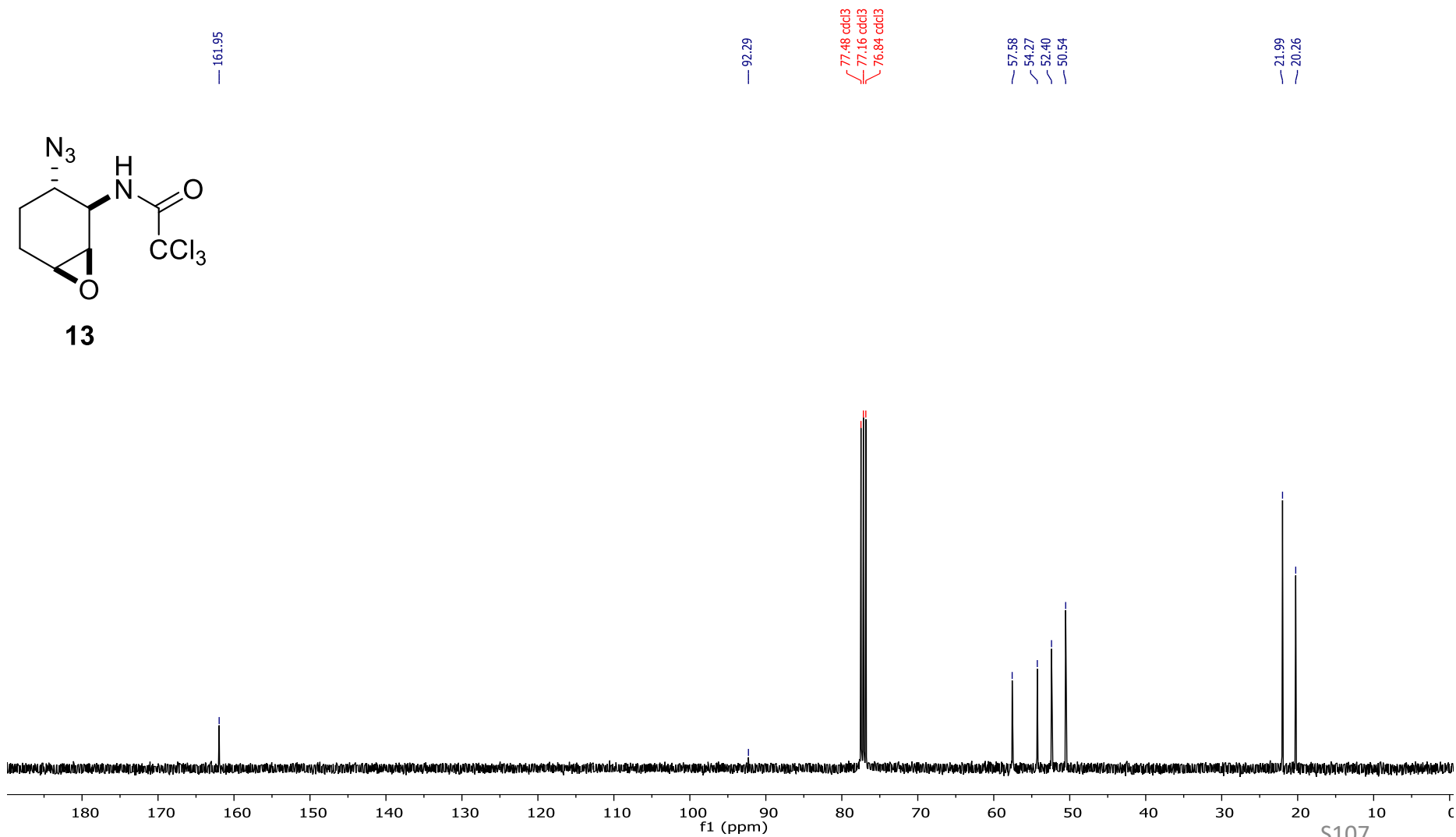
13



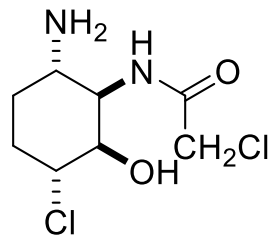
^{13}C NMR of Compound 13 (CDCl_3 ; 100 MHz)



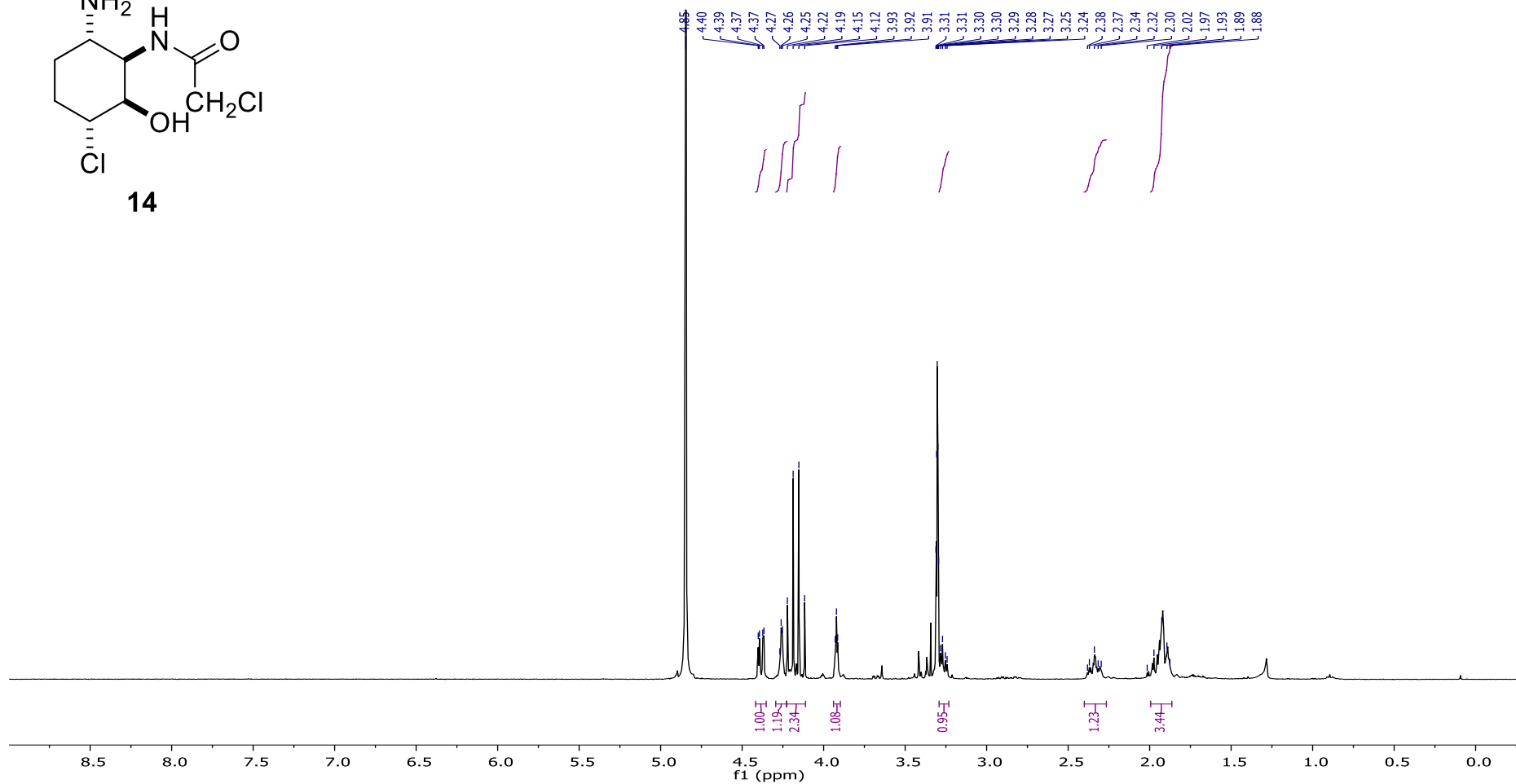
13



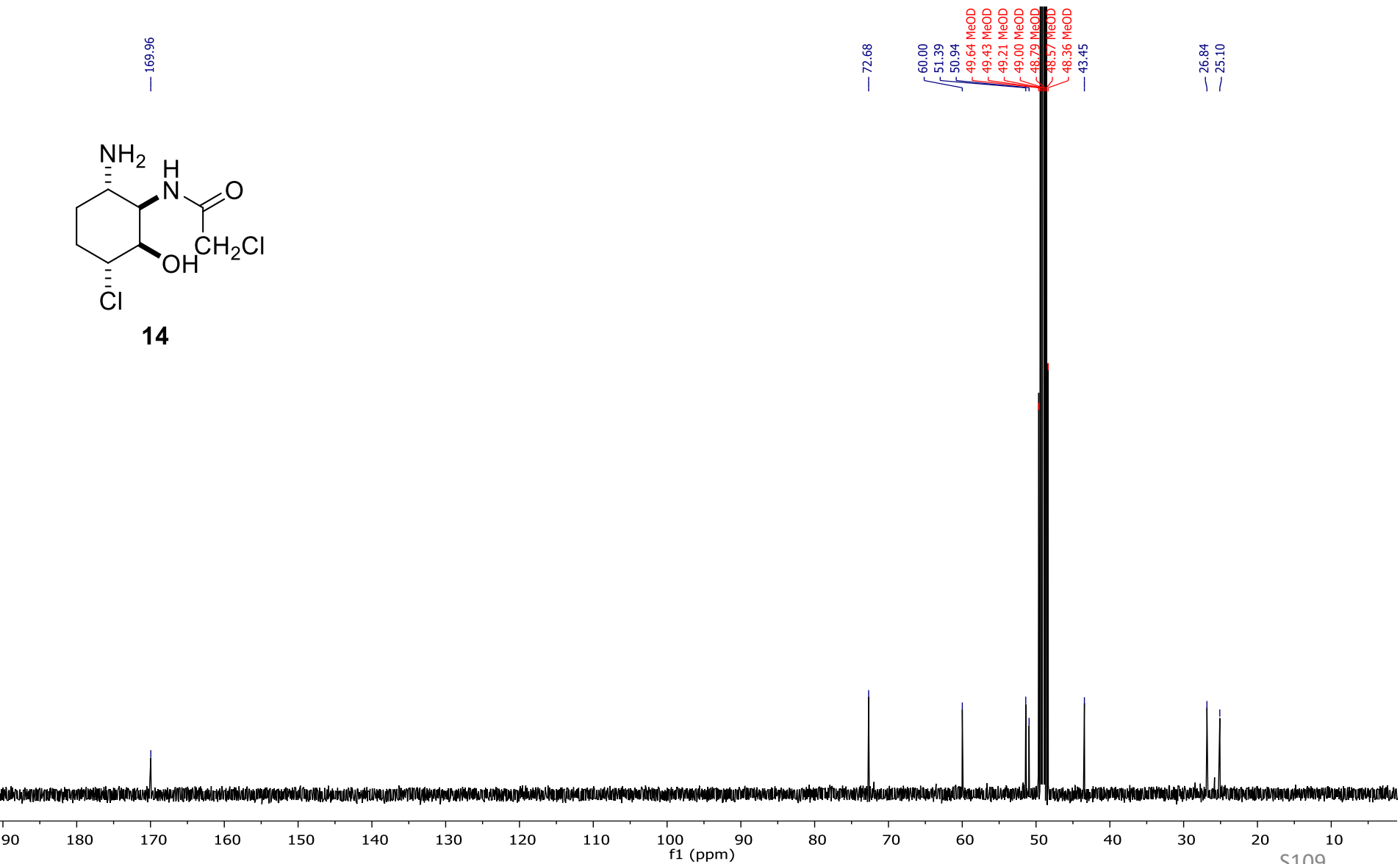
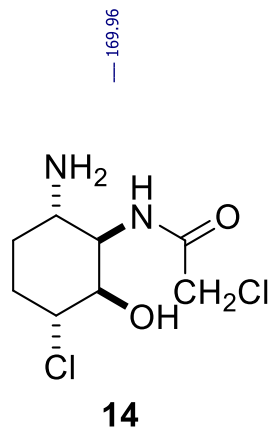
^1H NMR of Compound 14 (CD_3OD ; 400 MHz)



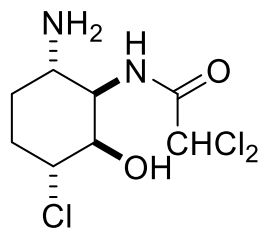
14



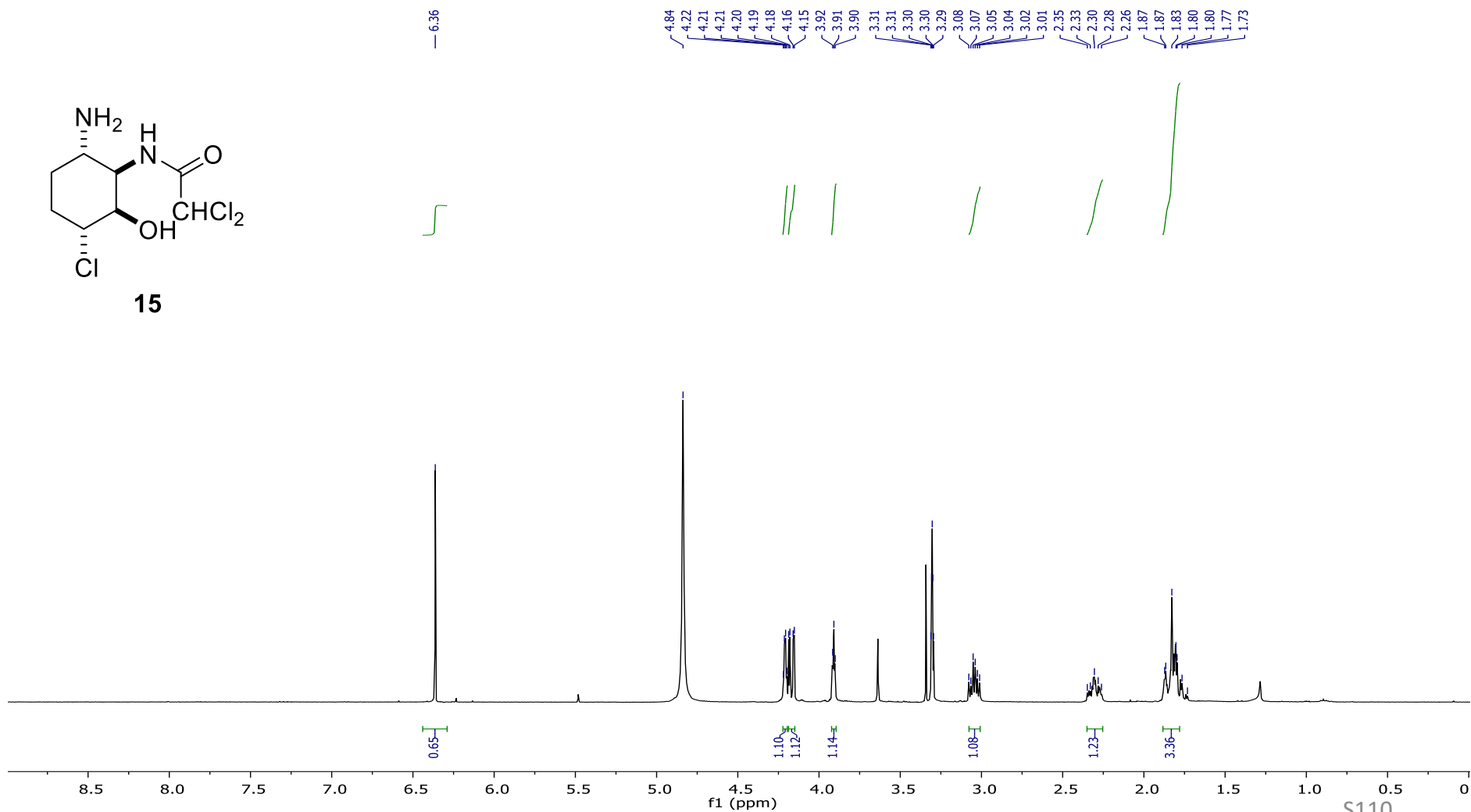
^{13}C NMR of Compound 14 (CD_3OD ; 100 MHz)



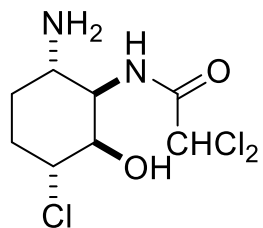
^1H NMR of Compound 15 (CD_3OD ; 400 MHz)



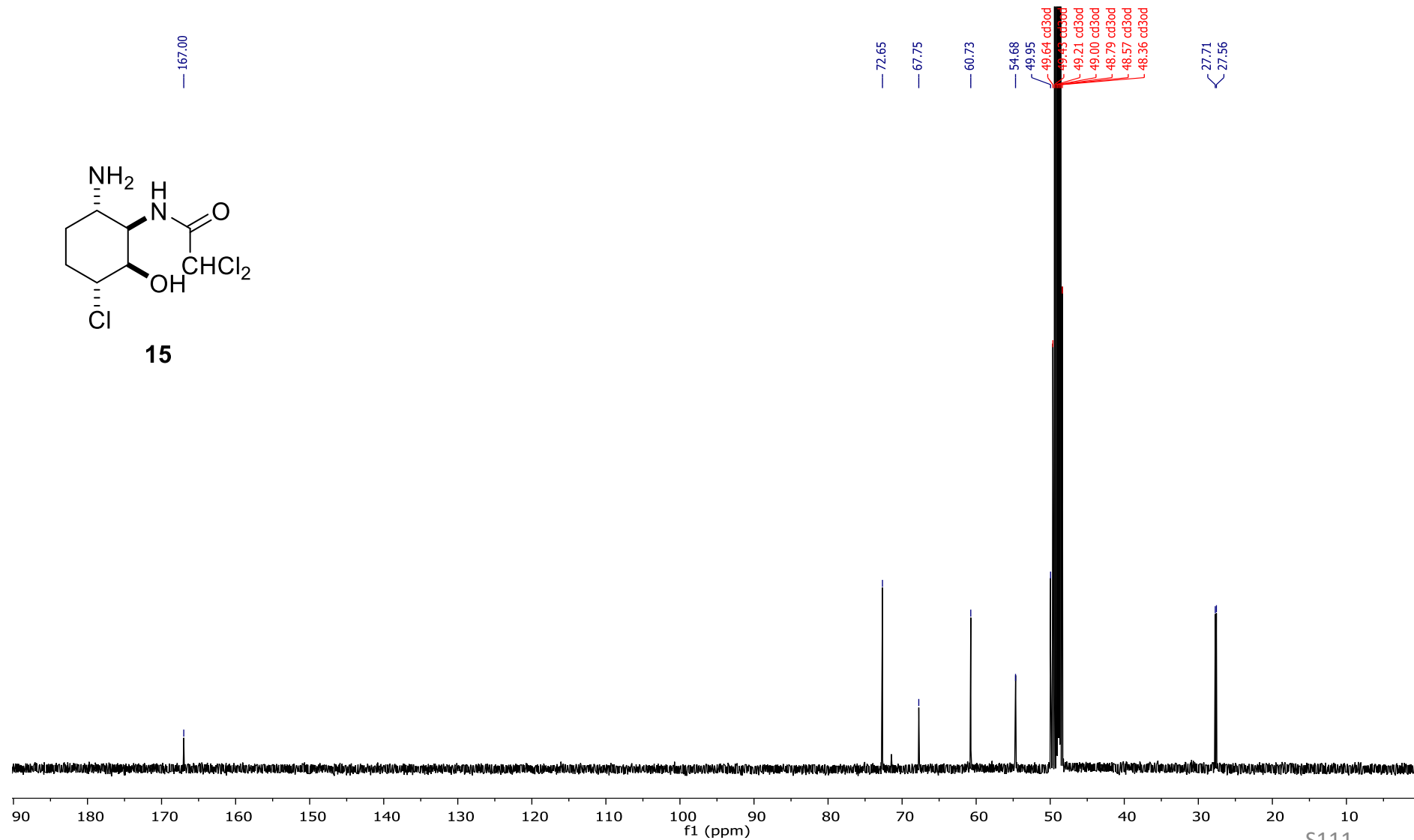
15



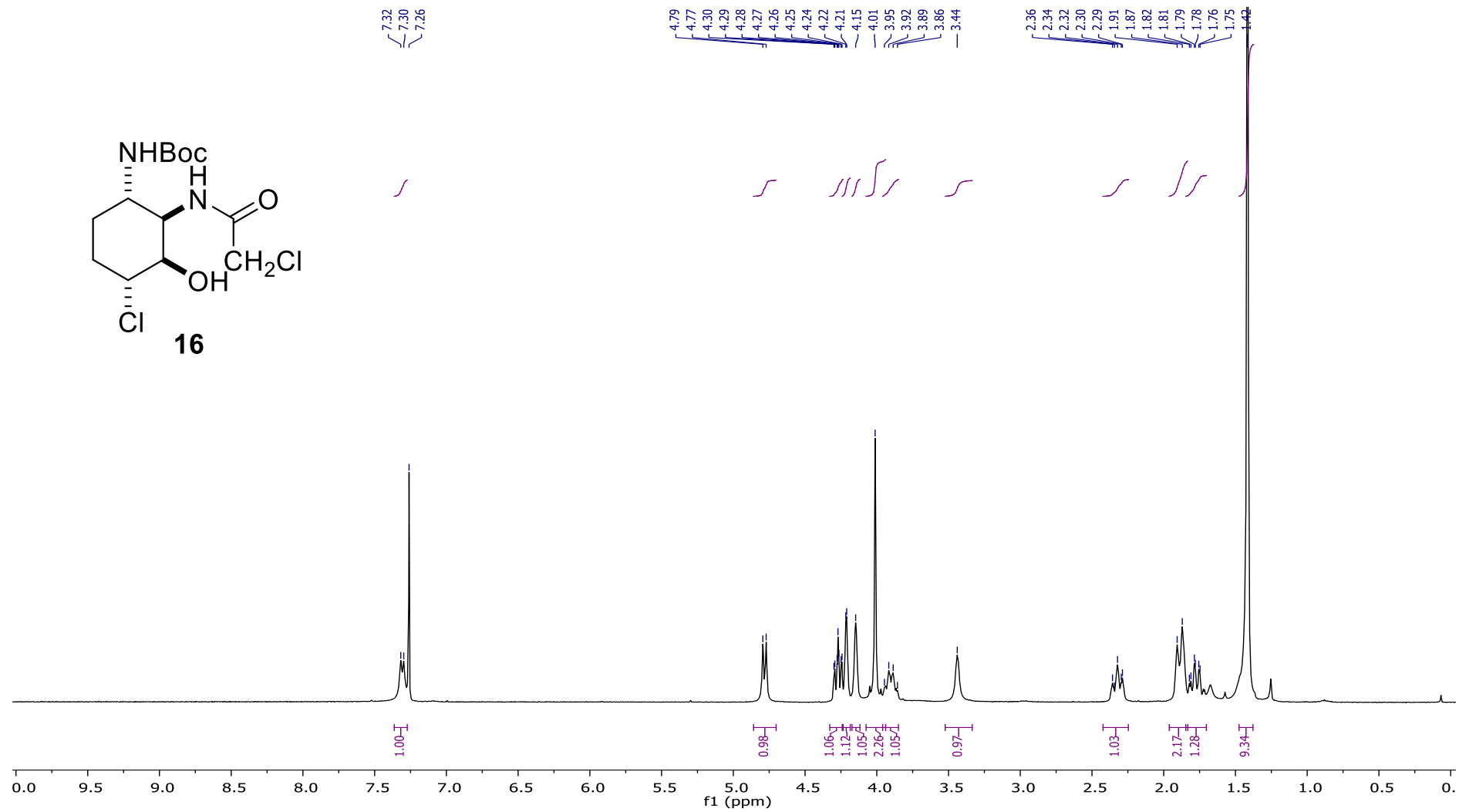
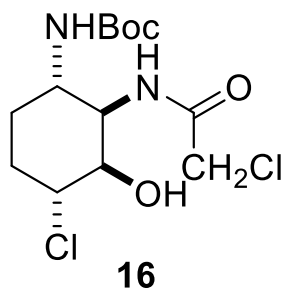
¹³C NMR of Compound 15 (CD₃OD; 100 MHz)



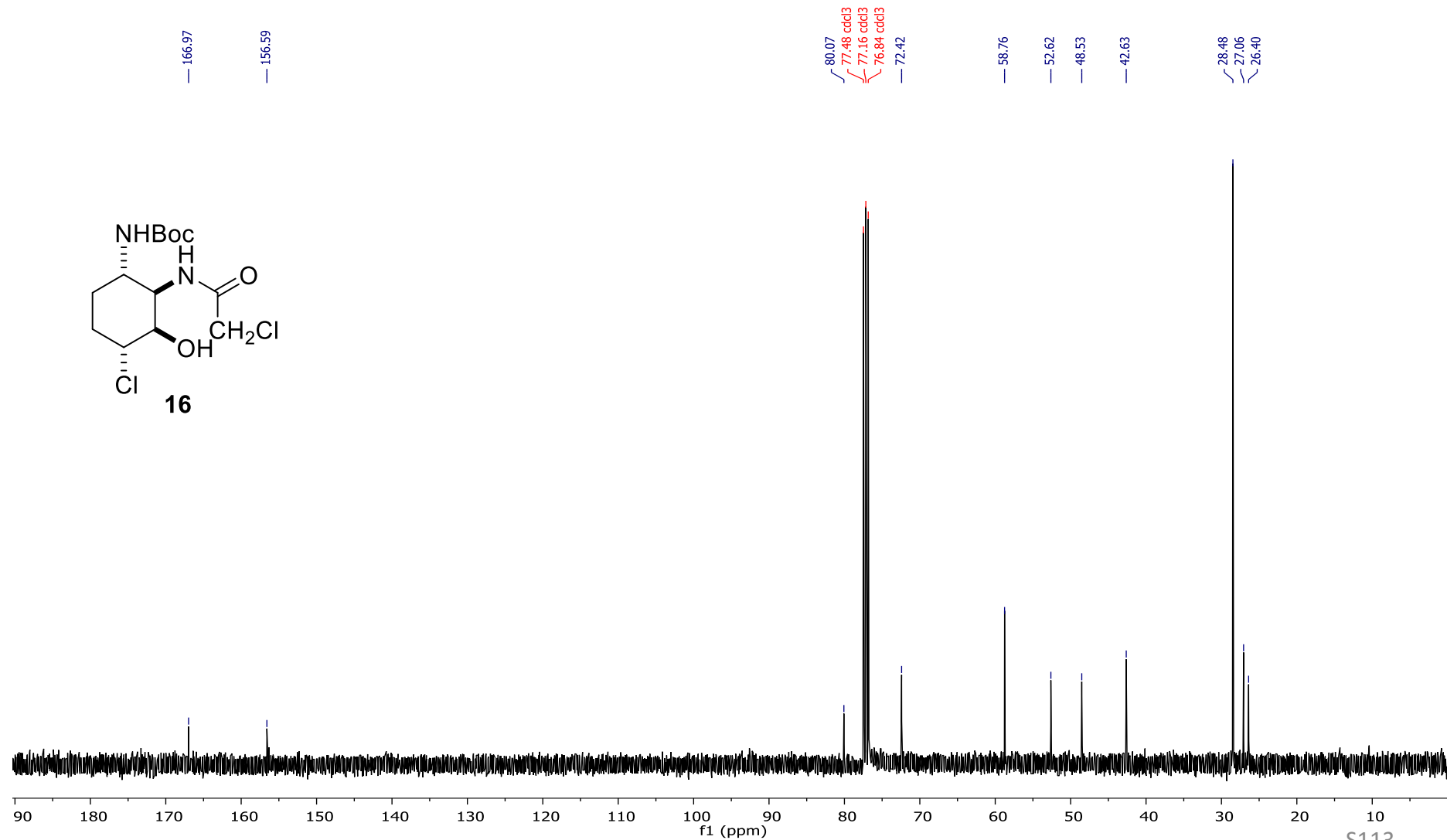
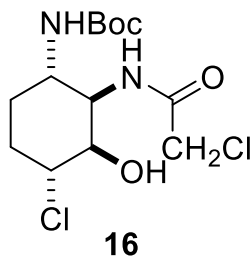
15



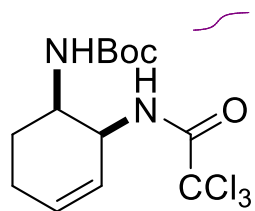
^1H NMR of Compound 16 (CDCl_3 ; 400 MHz)



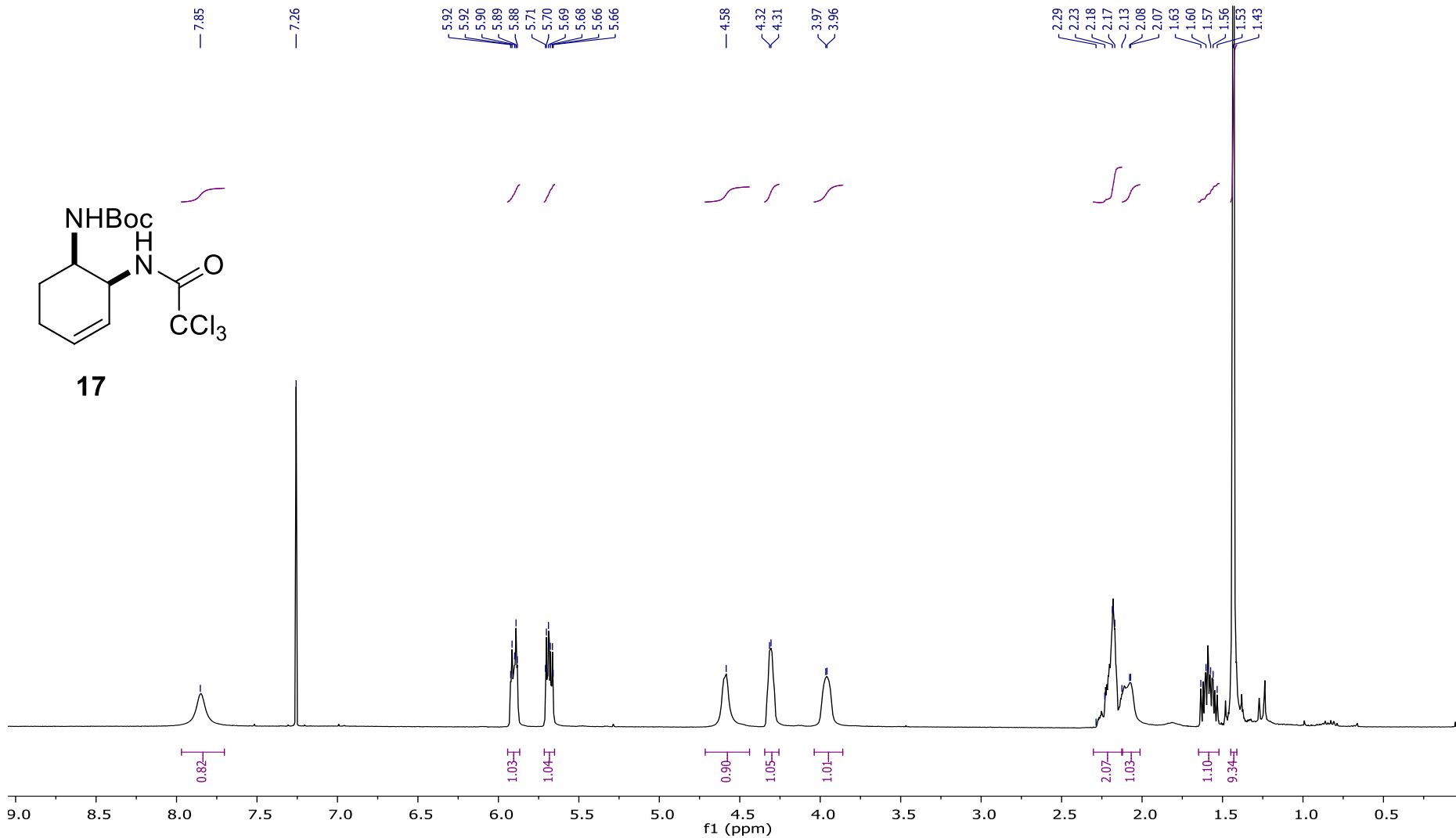
^{13}C NMR of Compound 16 (CDCl_3 ; 100 MHz)



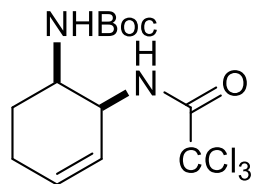
¹H NMR of Compound 17 (CDCl₃; 400 MHz)



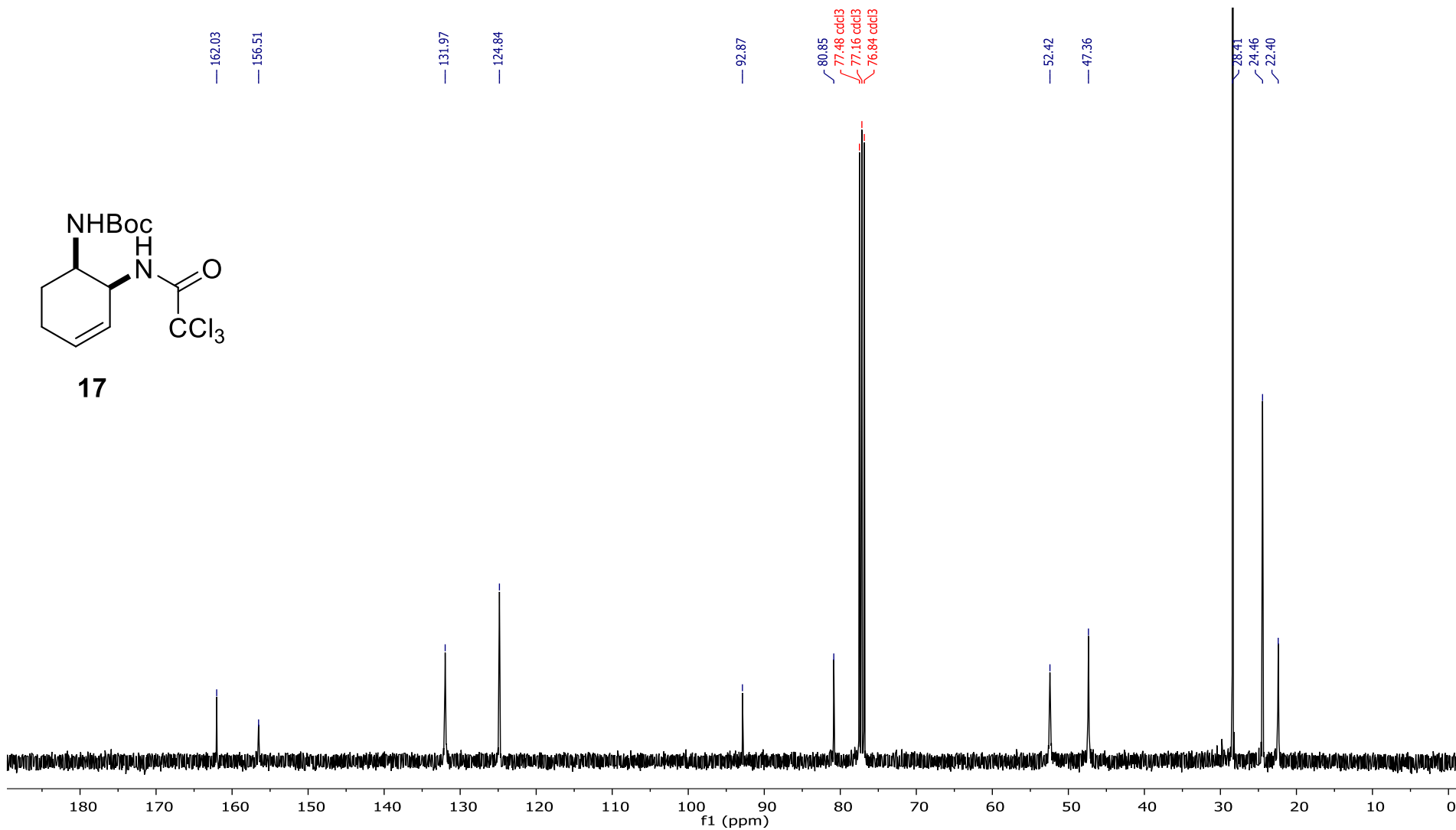
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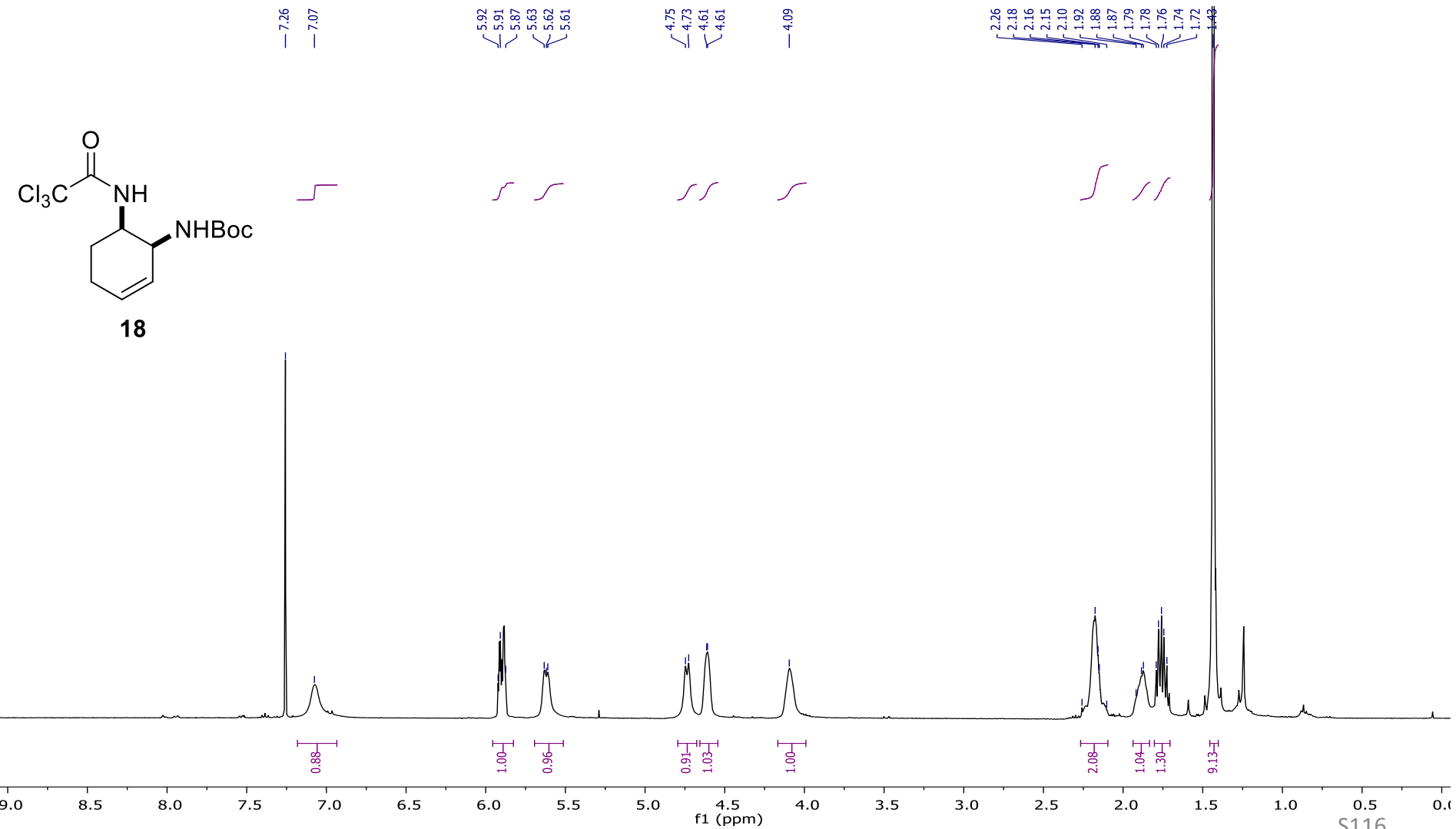
^{13}C NMR of Compound 17 (CDCl_3 ; 100 MHz)



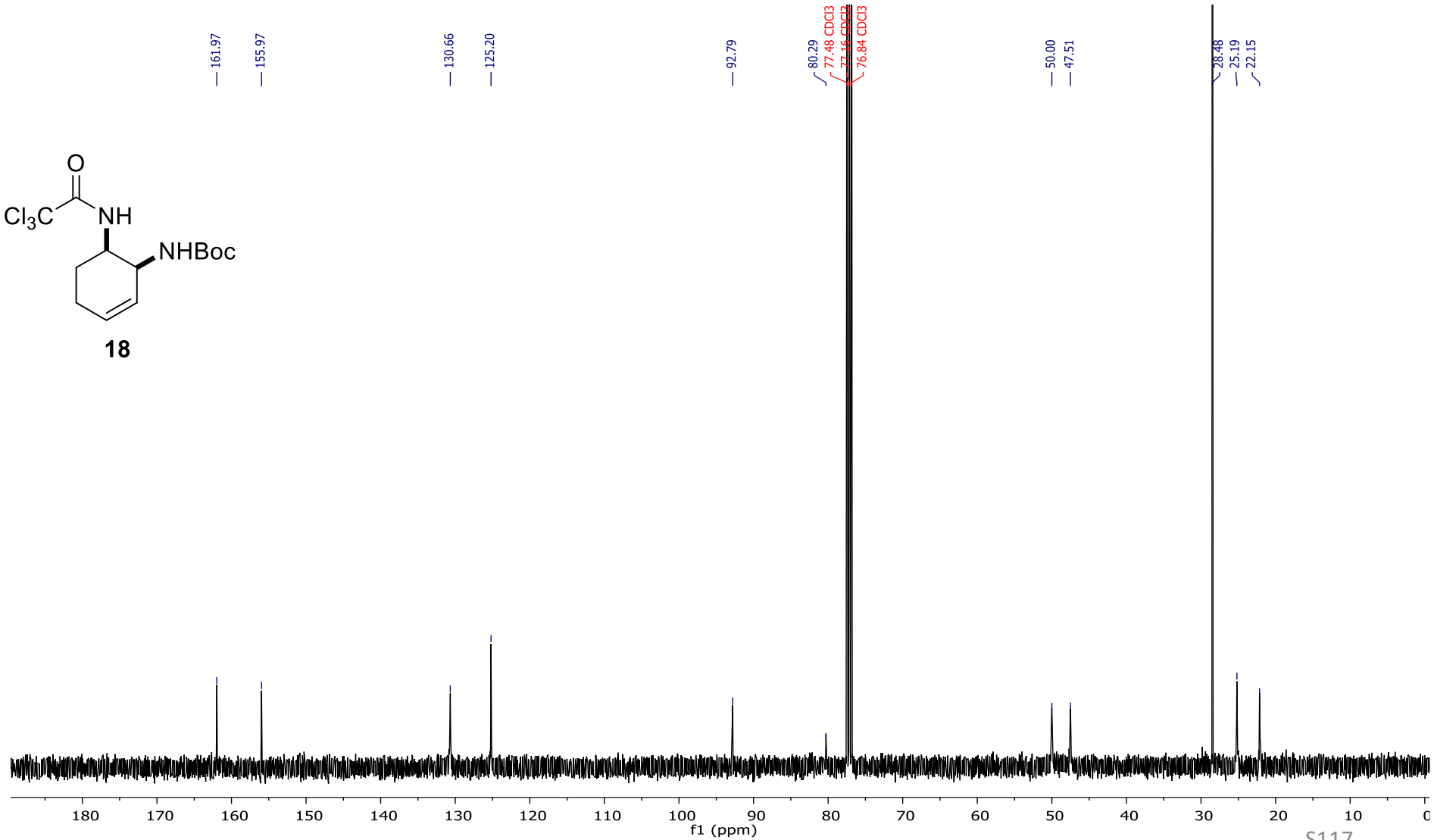
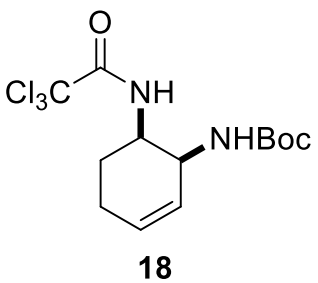
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¹H NMR of Compound 18 (CDCl₃; 400 MHz)

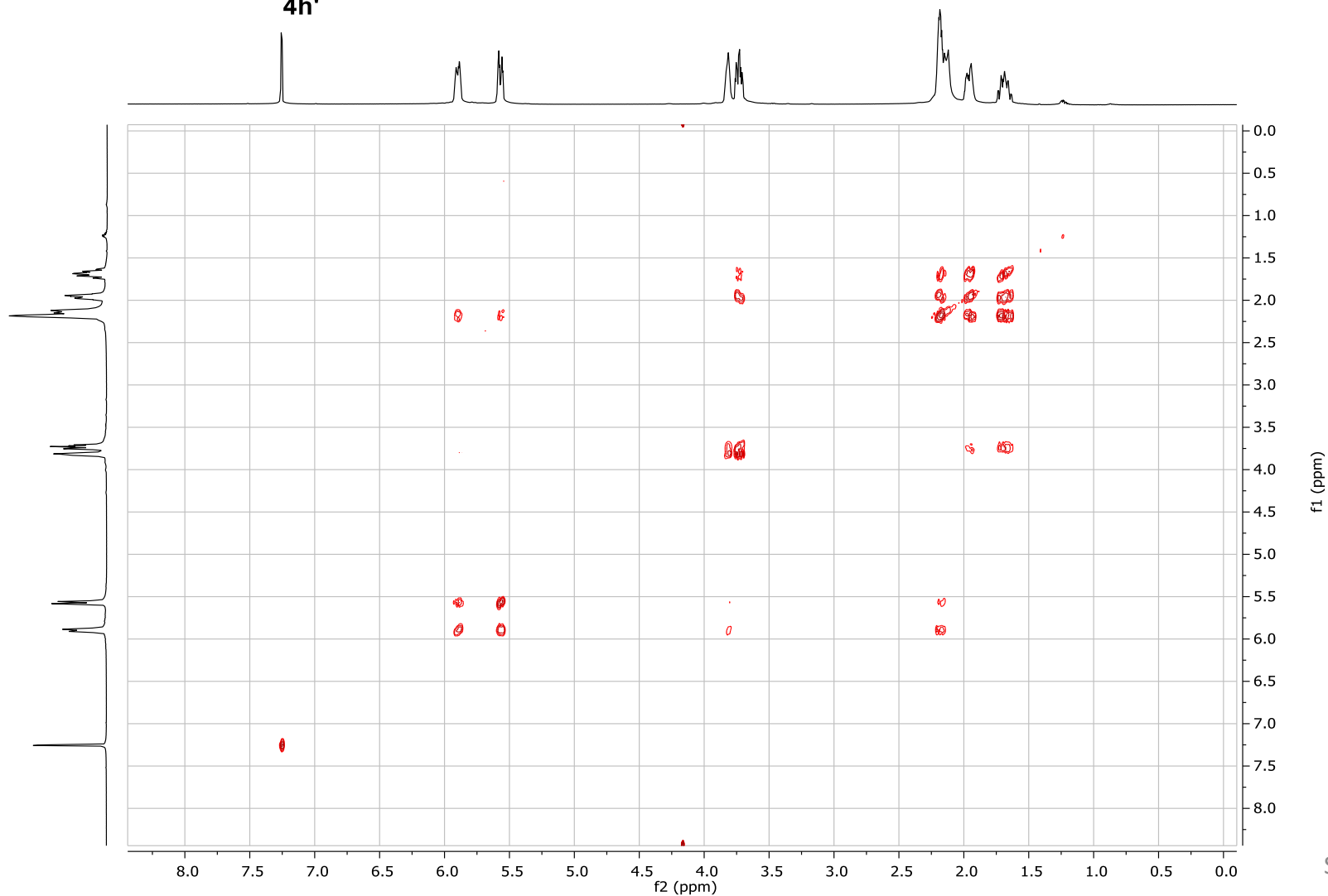
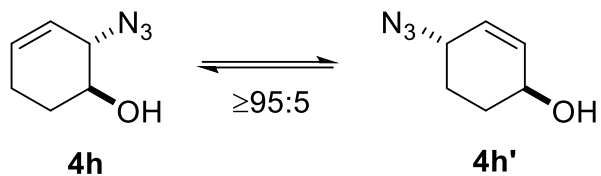


¹³C NMR of Compound 18 (CDCl₃; 100 MHz)

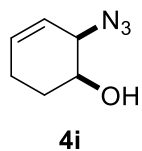


Selected 2D-Spectra

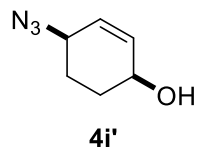
^1H - ^1H COSY spectrum (400 MHz) of 4h and 4h' in CDCl_3

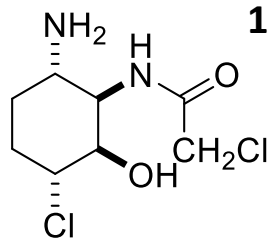


^1H - ^1H COSY spectrum (400 MHz) of 4i and 4i' in CDCl_3



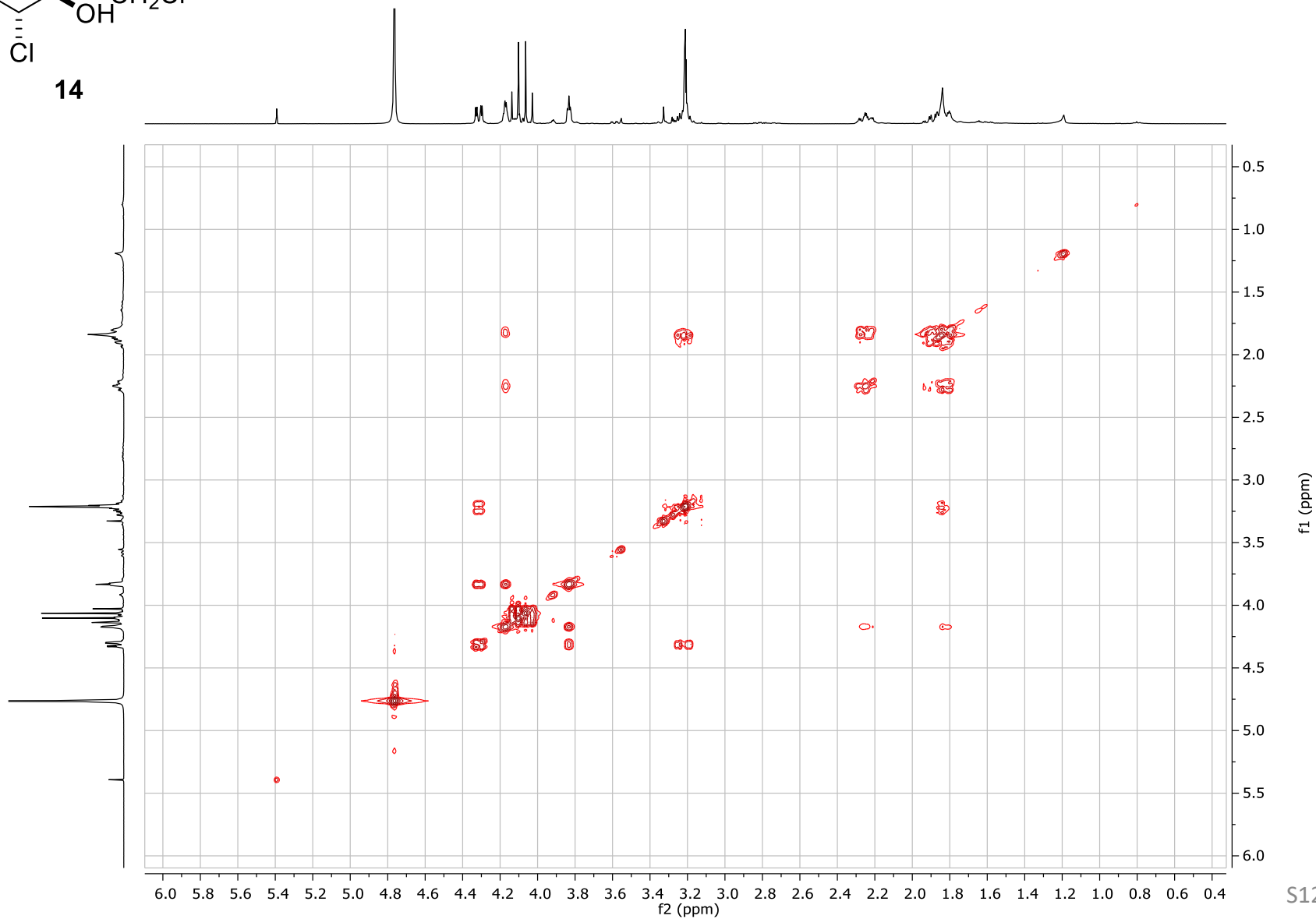
80:20

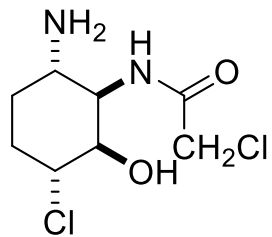




14

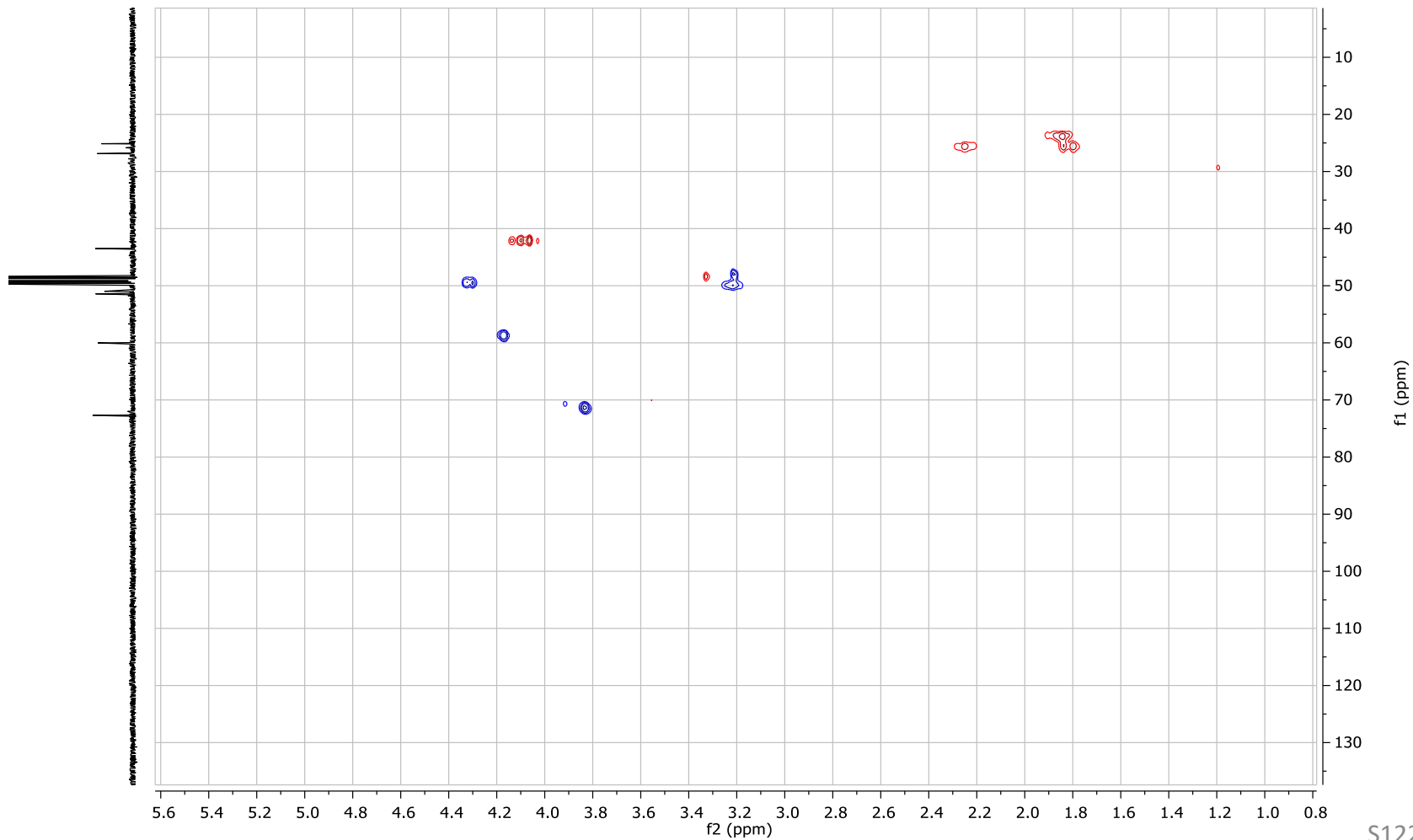
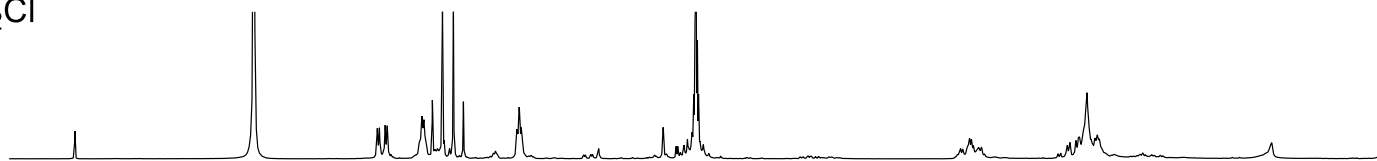
¹H-¹H COSY spectrum (400 MHz) of 14 in CD₃OD



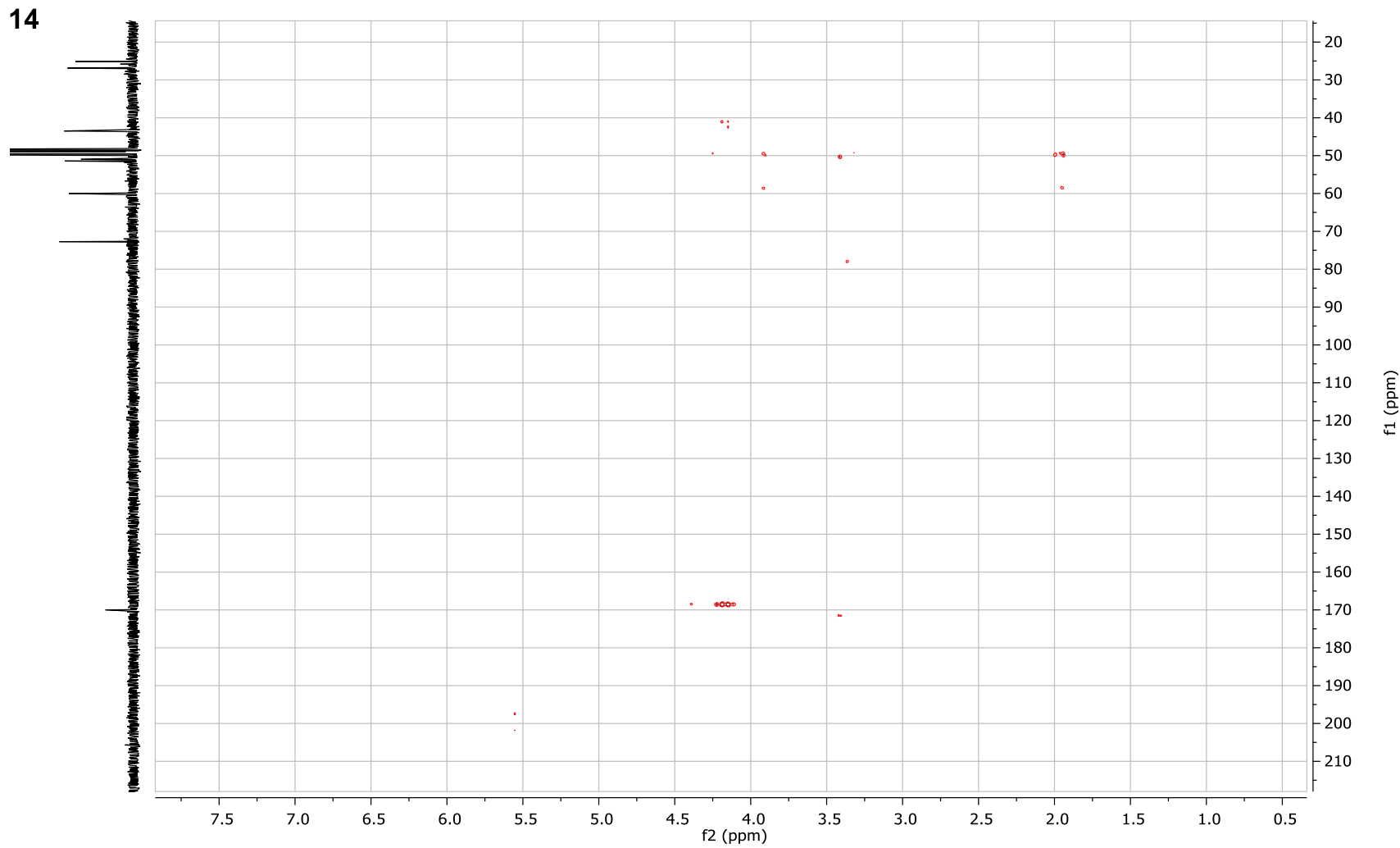
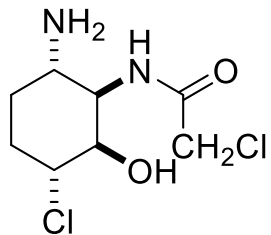


14

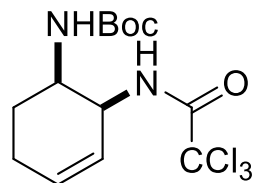
HSQC spectrum (400 MHz) of 14 in CD₃OD



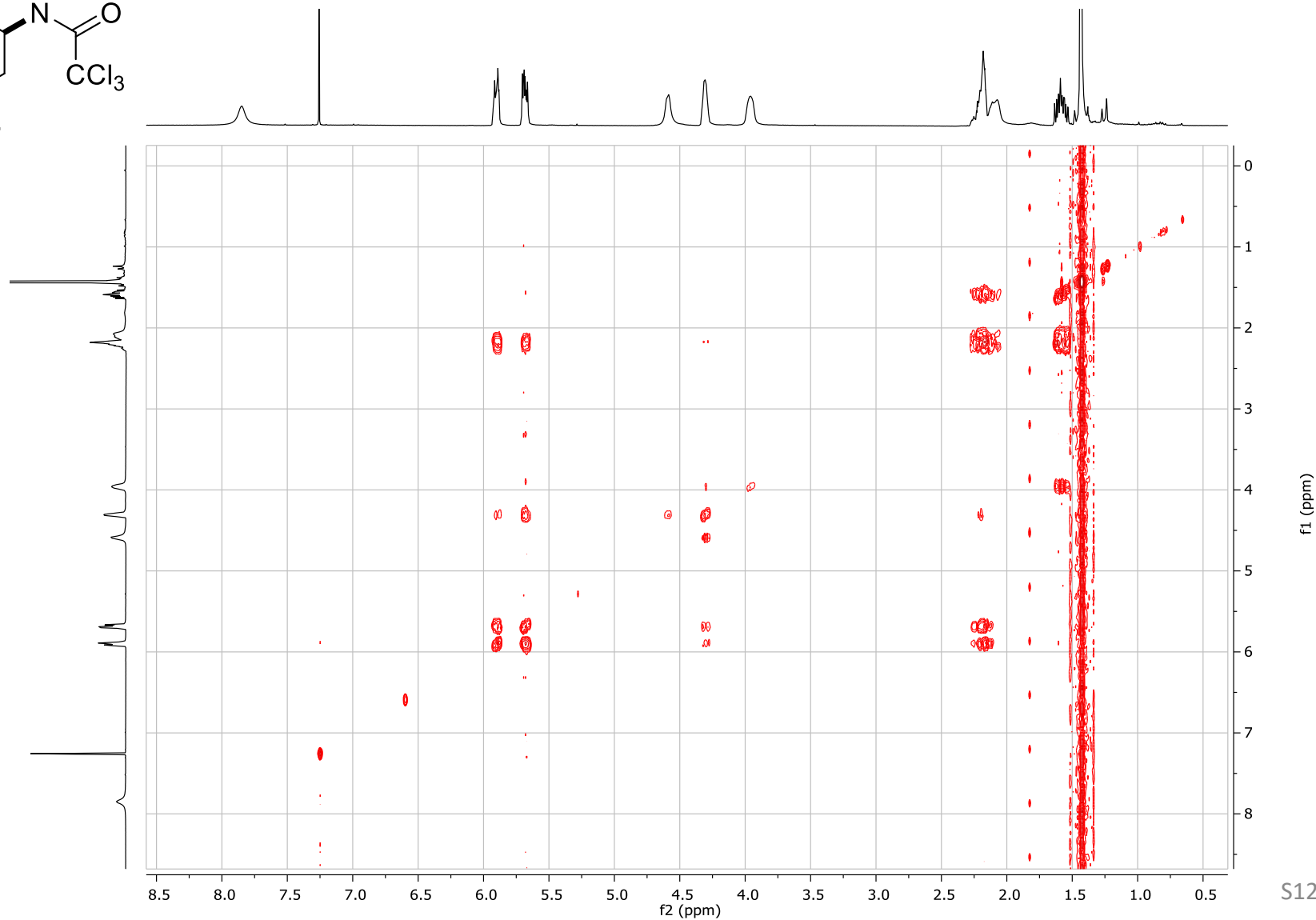
HMBC spectrum (400 MHz) of 14 in CD₃OD



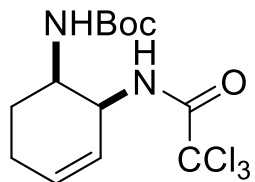
^1H - ^1H COSY spectrum (400 MHz) of 17 in CDCl_3



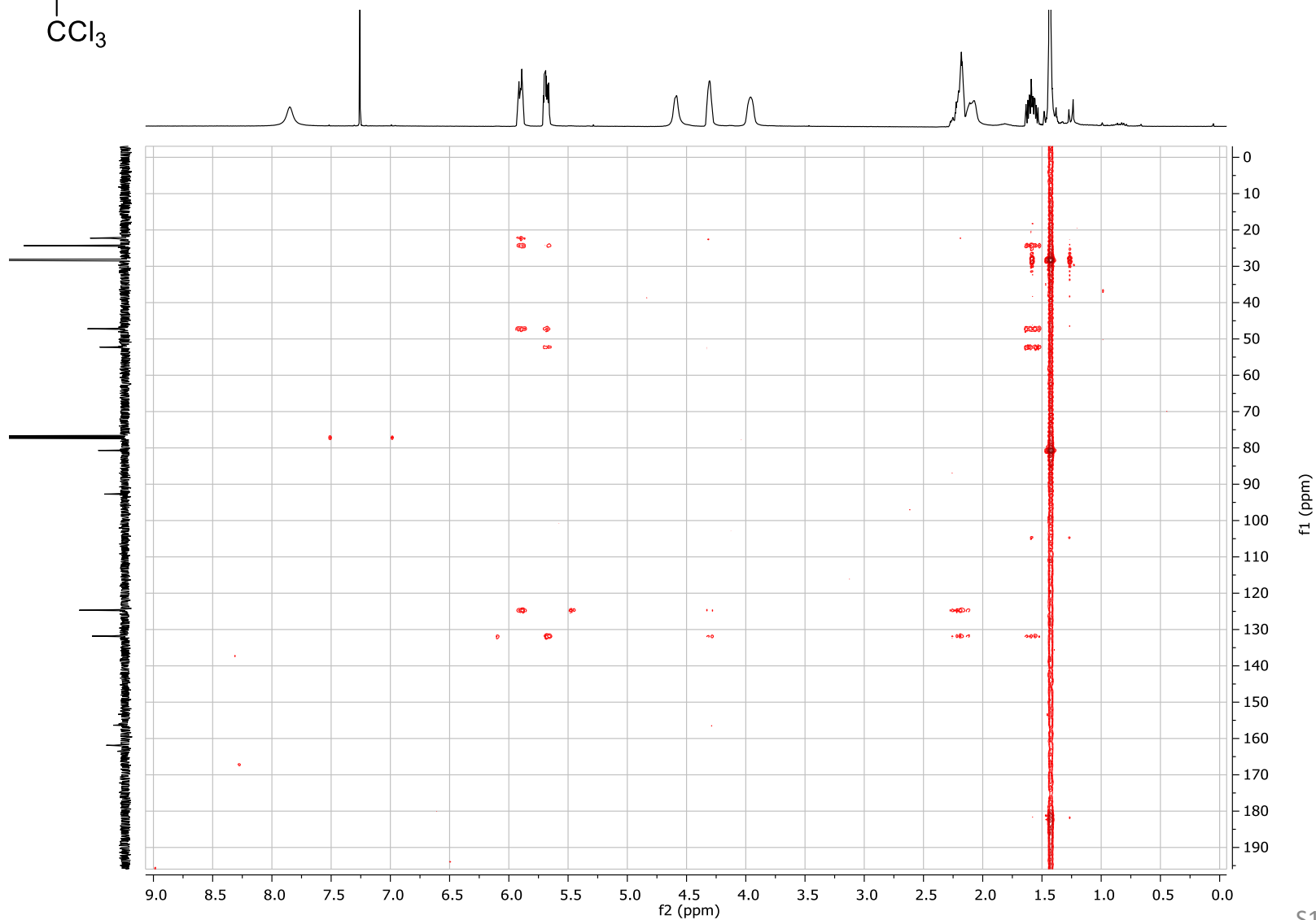
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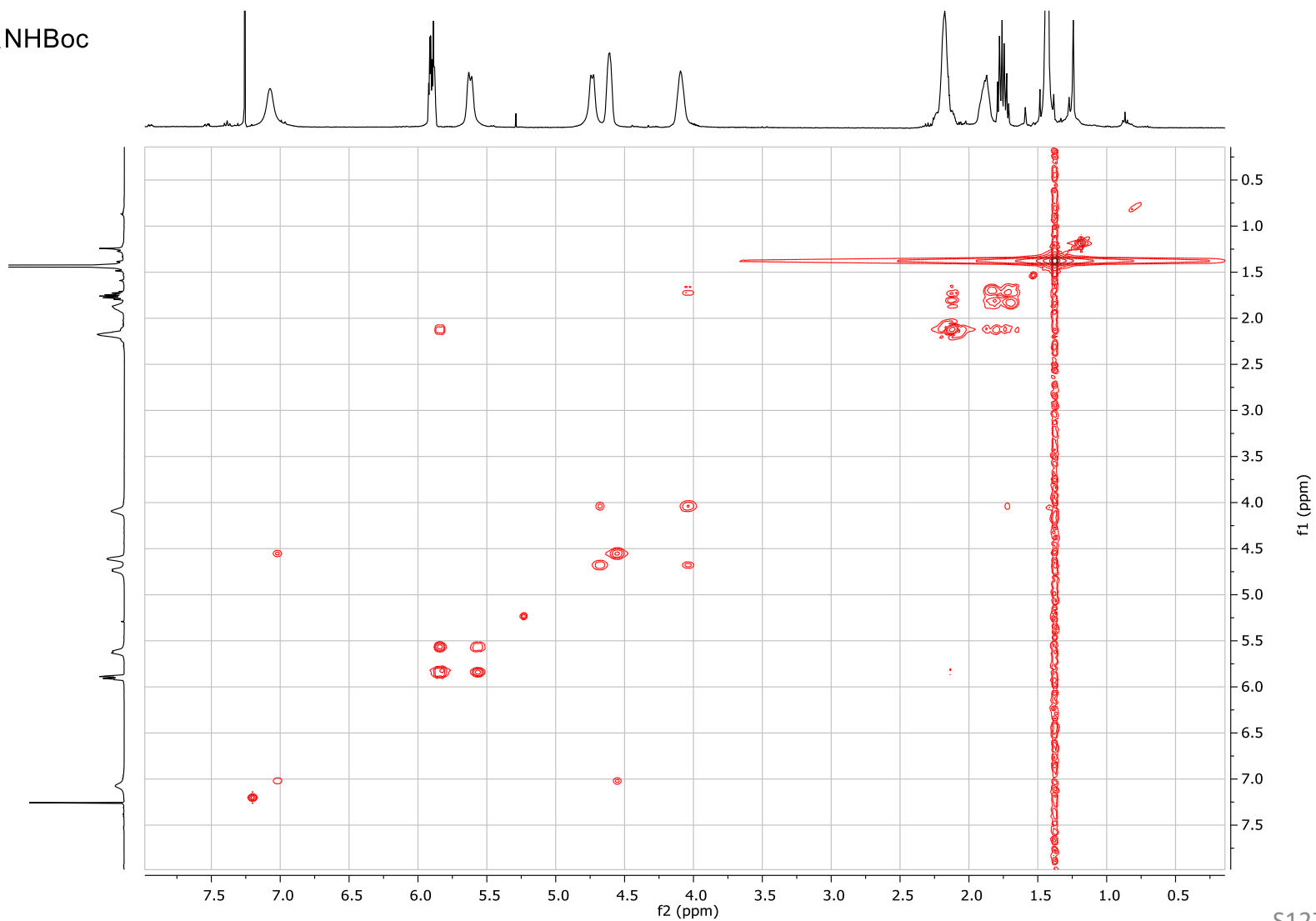
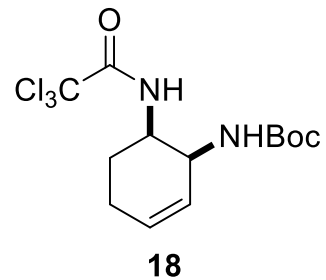
HMBC spectrum (400 MHz) of 17 in CDCl₃



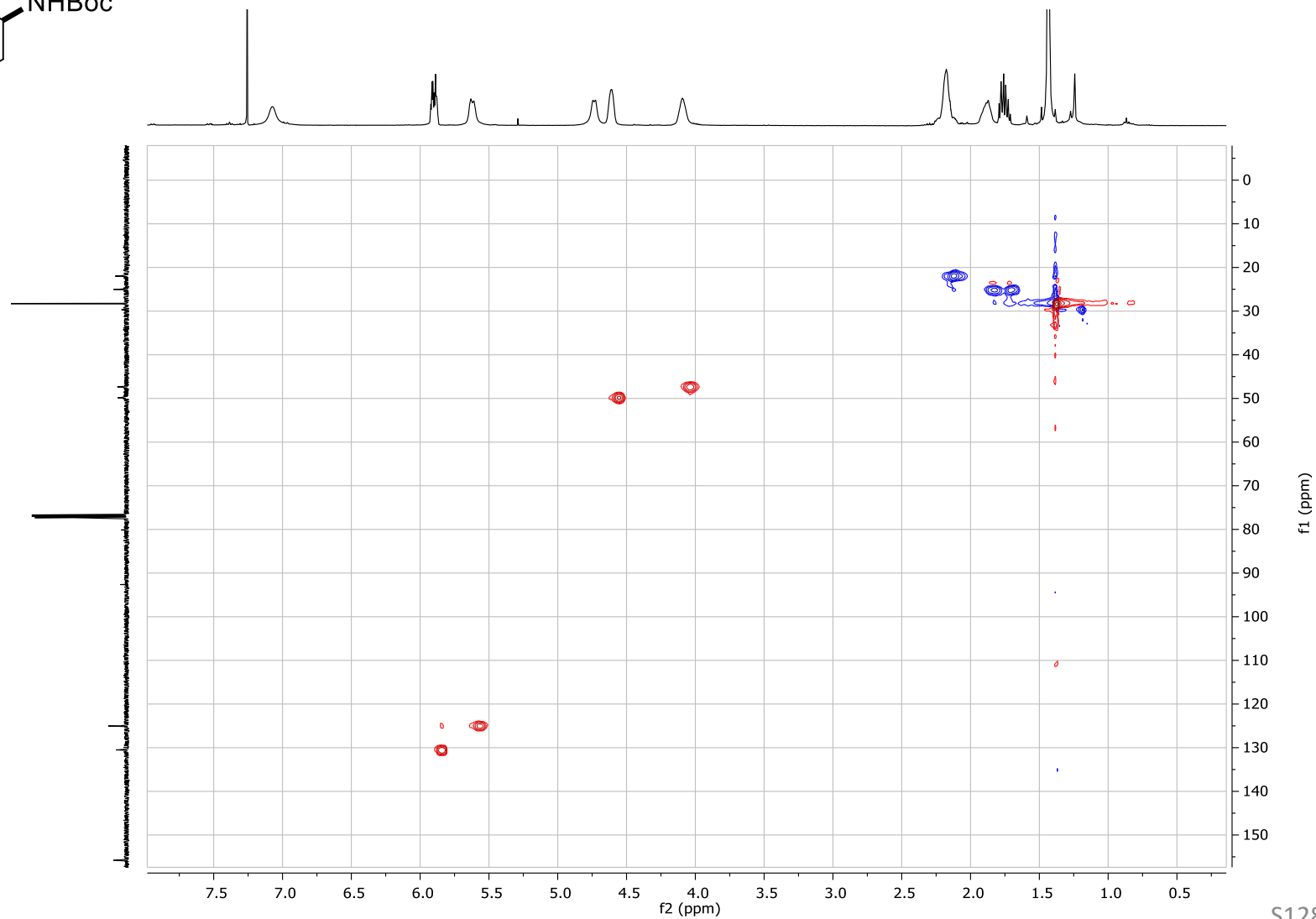
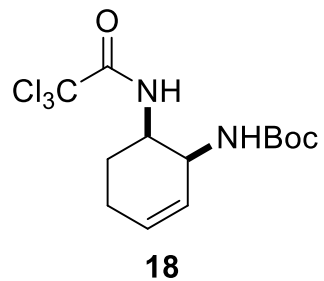
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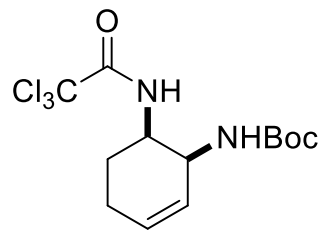
^1H - ^1H COSY spectrum (400 MHz) of 18 in CDCl_3



HSQC spectrum (400 MHz) of 18 in CDCl₃



HMBC spectrum (400 MHz) of 18 in CDCl₃



18

