

Supporting Information

Optimization of Enantioselection Using a Modular Oxazoline catalyst: Application to a Hydrogen Bond Promoted Hetero Diels-Alder Reaction

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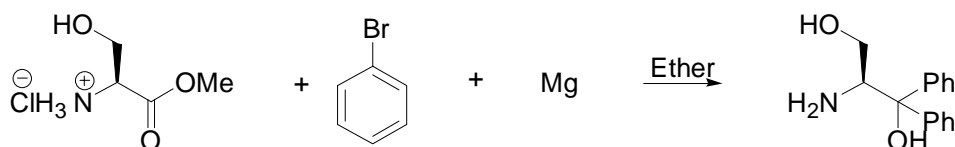
General Methods:

Unless otherwise noted all reactions were performed under an argon atmosphere with stirring. Dichloroethane was distilled from CaH₂. Methanol was distilled from magnesium methoxide.¹ Cbz amino acids were obtained from advanced chemtech and used without further purification. Triethylamine was distilled from CaH₂ prior to use. N-methyl morpholine and isobutyl chloroformate were purchased from Acros and used without further purification. Methanesulfonyl chloride was purchased from Acros and used without purification. All the other sulfonyl chlorides were obtained from Aldrich. (*S*)-10-Camphorsulfonyl chloride was recrystallized from a mixture of toluene and hexanes. DMAP was recrystallized from toluene.¹ Flash chromatography was performed using EM Reagent silica 60 (230-400 mesh). Analytical thin layer chromatography was performed with Whatman K6F Silica 60 Å plates. IR spectra were recorded using a Mattson Satellite FTIR instrument. NMR spectra were recorded using one of the following: (i) Varian Unity-300 Spectrometer, (ii) Varian XL-300 Spectrometer, (iii) Varian VXR-500 Spectrometer. HRMS were recorded using a Finnigan MAT 95 spectrometer. Optical rotations were recorded on Perkin Elmer Model 343 Polarimeter. All melting points are uncorrected and recorded on Thomas Hoover Unimelt capillary melting point apparatus. All the pyranones have been reported previously in literature.^{2,3}

Purification of *p*-Toluenesulfonyl chloride:¹

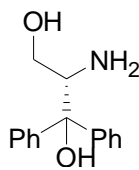
Approximately 10g of *p*-toluenesulfonyl chloride was dissolved in 25 mL of CHCl₃. To the resulting solution, 125 mL of pentane is added. After standing for 20 min, the solution was filtered to remove *p*-toluenesulfonic acid. The filtrate is concentrated to about 10 mL and on standing overnight crystals were obtained. The crystals were filtered, washed with pentane and dried overnight under high vacuum.

Synthesis of aminodiol:⁴

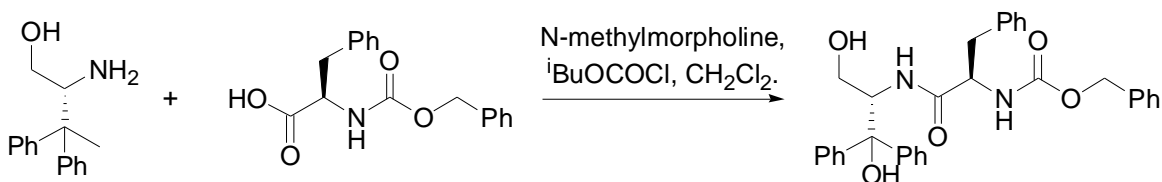


A 500 mL 2-neck flask fitted with a condenser and a pressure equalizing addition funnel is charged with 4.8 g of magnesium (197.5 mmol). The flask is flushed with argon and 20 mL of dry ether is added followed by 0.9 mL of bromobenzene and 5 drops of 1,2-dibromoethane. A vigorous reaction ensues and the solution turns to a yellowish brown color. To this solution, 20 mL of bromobenzene (196.5 mmol, total) dissolved in 180 mL of ether is added using the addition funnel such that a mild reflux is maintained

(~ 90 min). After completion of addition, the contents are allowed to stir until most of the magnesium is dissolved (~ 4h). The prepared Grignard reagent is then cannulated dropwise in to a flask containing a slurry of (*L*)-serine methylester hydrochloride in ether (5g in 100 mL of ether, ~45 min). The contents are stirred overnight (stirring might stop due to the formation of a gummy mixture at the bottom of the flask. This does not however, reduce the yield of the reaction). The reaction is then carefully quenched by the drop wise addition of 3N HCl (**caution**: reaction is exothermic. The volatility of ether may cause build up of pressure). The pH of the reaction mixture is adjusted to ~2 and excess water is added to get the undissolved solids into the aqueous phase. The organic layer is separated and the aqueous layer is washed with CH₂Cl₂ (2 X 100 mL). The organic layers are discarded. The pH of the aqueous layer is increased to ~12 by the addition of 2N NaOH and the aqueous layer is extracted with dichloromethane (4 X 100 mL, 1 X 50 mL). Formation of emulsion during these extractions can be alleviated by the addition of solid citric acid monohydrate. Care should be taken so that pH does not drop below 11). The combined organic layers are washed with brine (2 X 100 mL), dried over Na₂SO₄, and concentrated. The residue is redissolved in minimum amount of toluene and placed in a refrigerator overnight. The amino diol that crystallizes out of the solution is collected by filtration and washed with hexanes to obtain 4.22g of an off white solid (54%). On occasion the amino diol may fail to crystallize. If this occurs the toluene solution can be stored in a -20 °C freezer or a seed crystal may be added and the flask can be maintained at room temperature overnight. A third approach that has worked is triturating with hexanes.

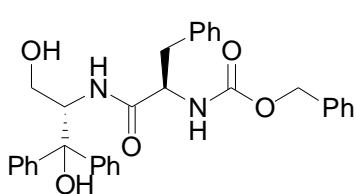

(5): mp: 88-89 °C; $[\alpha]_D^{20} = -113.1^\circ$ (c = 1, CHCl₃); IR (KBr) 3340, 3063, 2946, 1490, 1447, 1051, 1036 cm⁻¹; ¹H NMR (300 MHz CDCl₃) δ 2.28 (brs, 2H), 3.60 (m, 2H), 3.91 (m, 1H), 4.62 (brs, 1H), 7.17-7.36 (m, 6H), 7.49-7.51 (m, 2H), 7.55-7.58 (m, 2H); ¹³C NMR {¹H} (75 MHz, CDCl₃) δ 57.2, 63.5, 79.8, 125.4, 125.7, 127.0, 127.2, 128.6, 128.8, 144.9, 145.9; HRMS (CI, isobutane) m/z (M+H)⁺ calcd. 244.1338, obsd. 244.1340

Synthesis of β-hydroxyamides:⁵

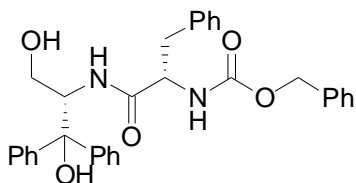


A 250 mL round bottom flask is charged with 2.7 g of Cbz-(*R*)-phenylalanine (9.02 mmol) and the flask is flushed with argon. It is dissolved in 45 mL of dry CH₂Cl₂ and 1.2 mL of N-methylmorpholine (99%, 10.8 mmol) is added. The flask is cooled to -15 °C with a NaCl, ice mixture and 1.4 mL of isobutylchloroformate (97%, 10.5 mmol) is added drop wise over 5 min. The contents are stirred at this temperature for 40 minutes after which, 2.5 g of the aminodiol **5** (10.4 mmol) dissolved in 10 mL of CH₂Cl₂ and 1.6 mL N-methylmorpholine is added via a cannula. A further 4 mL of CH₂Cl₂ is used for

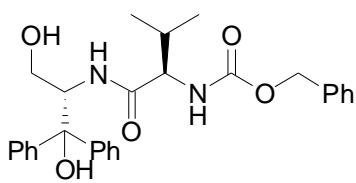
rinsing. The bath is allowed to warm up to room temperature, and the reaction mixture is stirred at room temperature for an hour. The contents are transferred to a separatory funnel and diluted with 50 mL of CH₂Cl₂. The organic layer is sequentially extracted with 1N HCl (50 mL), water (50 mL), and brine (50 mL). It is then dried over Na₂SO₄ and concentrated (use of a rotary evaporator without suction and setting the bath temperature at 60 °C works ideally). Recrystallization from refluxing toluene followed by washing with a 2:1 mixture of hexanes and toluene yields 4.27 g of a white solid (90%, average yield: 86%)



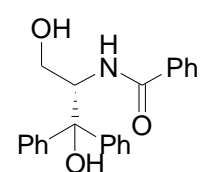
(6): mp: 158-159 °C; $[\alpha]_D^{20} = -15^\circ$ (c = 0.2, CHCl₃); IR (KBr) 3503, 3398, 3319, 1732, 1634, 1537, 1511, 1448, 1228, 1044, cm⁻¹; ¹H NMR (500 MHz CDCl₃) δ 2.09 (brs, 1H), 2.84-3.02 (m, 2H), 3.55-3.58 (m, 1H), 3.70 (brs, 1H), 4.27-4.3 (m, 1H), 4.73 (s, 1H), 4.88 (d, *J* = 3.9 Hz, 1H), 5.01 (m, 1H), 5.17 (d, *J* = 3.2 Hz, 1H), 6.65 (brs, 1H), 7.14-7.46 (m, 20H); ¹³C NMR {¹H} (125 MHz CDCl₃) δ 38.5, 54.6, 56.9, 62.9, 67.5, 81.2, 125.2, 125.4, 127.25, 127.3, 127.4, 128.3, 128.53, 128.55, 128.78, 128.82, 129.1, 129.4, 136.2, 136.6, 144.4, 145.2, 156.4, 170.9; HRMS (CI, isobutane) *m/z* (M+H)⁺ calcd. 525.2390, obsd. 525.2374



(7): Yield: 84%; White solid; mp: 178-180 °C; $[\alpha]_D^{20} = -81.1^\circ$ (c = 0.2, CHCl₃); IR (KBr) 3403, 3328, 3319, 1702, 1656, 1524, 1259, 1239, 1061, cm⁻¹; ¹H NMR (300 MHz CDCl₃, 40 °C) δ 2.75 (d, *J* = 3.2 Hz, 2H), 3.05 (brs, 1H), 3.68 (d, *J* = 5.9 Hz, 1H), 3.85 (d, *J* = 5.4 Hz, 1H), 4.24-4.32 (m, 1H); 4.76 (brs, 1H), 4.93, (d, *J* = 4.2 Hz, 1H), 4.99 (s, 2H), 5.3 (t, *J* = 5.2 Hz, 1H), 6.83 (brs, 1H), 6.94-6.97 (m, 2H), 7.13-7.34 (m, 14H), 7.45-7.52 (m, 4H); ¹³C NMR {¹H} (125 MHz CDCl₃) δ 38.2, 55.2, 56.7, 62.9, 67.5, 81.2, 125.3, 125.5, 127.1, 127.2, 127.3, 128.2, 128.4, 128.6, 128.7, 128.8, 129.3, 136.2, 136.4, 144.8, 145.3, 156.7, 171.8; HRMS (CI, isobutane) *m/z* (M+H)⁺ calcd. 525.2390, obsd. 525.2400



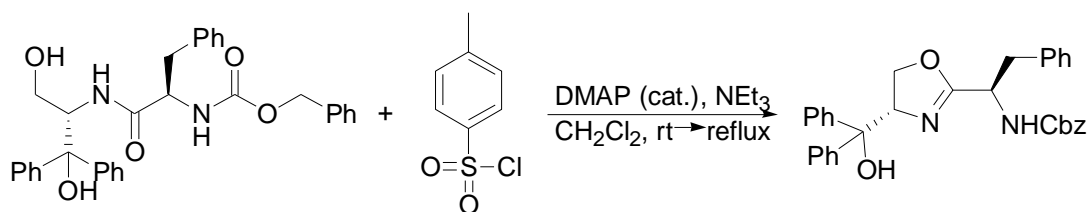
(8): Yield: 87%; White solid; mp: 160-161 °C; $[\alpha]_D^{20} = -9.7^\circ$ (c = 0.29, CHCl₃); IR (KBr) 3461, 3336, 1670, 1535, 1450, 1288 cm⁻¹; ¹H NMR (500 MHz CDCl₃) δ 0.65 (d, *J* = 3.4 Hz, 3H), 0.83 (d, *J* = 3.4 Hz, 3H), 2.06-2.20 (m, 1H), 2.7 (s, 1H), 3.70-3.73 (m, 1H), 3.88-3.95 (m, 2H), 4.89-4.93 (m, 2H), 5.04 (d, *J* = 2.9 Hz, 1H), 5.07 (s, 2H), 6.88 (d, *J* = 4.4 Hz, 1H), 7.13 (dd, *J* = 7.3 Hz, *J* = 7.6 Hz, 1H), 7.2-7.4 (m, 10H), 7.47 (d, *J* = 3.4 Hz, 2H), 7.52 (d, *J* = 3.9 Hz, 2H); ¹³C NMR {¹H} (125 MHz CDCl₃) δ 17.3, 19.4, 30.1, 55.2, 61.5, 62.6, 67.6, 81.0, 125.3, 125.4, 127.2, 127.3, 128.3, 128.5, 128.6, 128.8, 128.9, 136.1, 144.7, 145.2, 157.2, 171.1; HRMS (CI, isobutane) *m/z* (M+H)⁺ calcd. 477.2390, obsd. 477.2410



(9): Yield: 30%, white solid, analytically pure sample was obtained by chromatography; mp: 209-212 °C; $[\alpha]_D^{20} = -58.1^\circ$ (c = 0.1, CHCl₃); IR (KBr) 3371, 1637, 1536, 1490, 1063 cm⁻¹; ¹H NMR (300 MHz CD₃OD) δ 3.71-3.79 (m, 2H), 5.26 (dd, *J* = 4.0 Hz, *J* = 5.5 Hz, 1H), 7.08-7.64 (m

15H); ^{13}C NMR $\{^1\text{H}\}$ (75 MHz, CD_3OD) δ 61.5, 66.0, 84.3, 129.2, 129.4, 130.5, 130.6, 130.9, 131.8, 132.1, 132.2, 135.3, 138.8, 149.4, 149.9, 173.5; HRMS (CI, isobutane) m/z (M+H) $^+$ calcd. 348.1600, obsd. 348.1602

Synthesis of oxazolines:⁶



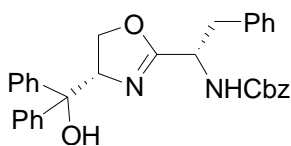
A 100 mL RB flask is charged with 2.076 g (3.94 mmol) of β -hydroxyamide **6**, and 49 mg of DMAP (0.4 mmol, 10 mol%). The flask is flushed with argon and 30 mL of dry dichloroethane (DCE) is added followed by 2.2 mL of freshly distilled triethylamine. In a separate flask, 715 mg of *p*-toluenesulfonyl chloride (3.75 mmol, 0.95 eq.) is dissolved in 10 mL of DCE and cannulated into the flask containing the β -hydroxyamide at room temperature. A further 5 mL of DCE is used for rinsing. The contents are stirred at room temperature, till formation of the tosylate is complete (by TLC. 50% ethyl acetate in hexanes. β -hydroxyamide, R_f = 0.23; tosylate, R_f = 0.53;). After complete conversion, the contents are refluxed till the conversion of the tosylate to the oxazoline is complete (by TLC 12-16h, 50% ethyl acetate in hexanes. oxazoline, R_f = 0.63;). On completion, the reaction mixture is diluted with 25ml of CH_2Cl_2 and washed with saturated aqueous NaHCO_3 (2 X 40 mL). The organic layer is dried over Na_2SO_4 and concentrated

Column chromatography:

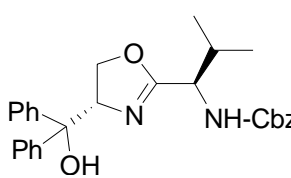
Approximately, 100 mL of SiO_2 is packed into a column with a 1:2 mixture of ether and hexanes as the solvent. The residue from work up is dissolved in minimum amount of CH_2Cl_2 and loaded on to the column. After an initial elution of 8 fractions (18 X 150 test tubes) with a 1:2 mixture of ether and hexanes as the solvent, the eluting solvent is switched to a 1:1 mixture of ether and hexanes. Fractions 7-17 were concentrated to yield 1.453 g of the oxazoline as a white solid (73% from β -hydroxyamide, average yield 72%).

(1g): mp: 120-123 °C; $[\alpha]_D^{20}$ = -9.6° (c = 0.31, CHCl_3), IR (KBr) 3436, 3352, 3031, 1701 1685 1657, 1532 1059 cm^{-1} ; ^1H NMR (500 MHz CDCl_3) δ 3.00 (dd, J = 8.1 Hz, J = 13.9 Hz, 1H), 3.20 (dd, J = 5.2 Hz, J = 14 Hz, 1H), 3.27(s, 1H), 4.18 (dd, J = 9.2 Hz, J = 9.2 Hz, 1H), 4.31 (dd, J = 7.7 Hz, J = 7.7 Hz, 1H), 4.61 (dd, J = 7.4 Hz, J = 13.3 Hz, 1H), 4.73 (d, J = 6 Hz, 1H), 4.99 (d, J = 5.9 Hz, 1H), 5.16 (d, J = 3.2 Hz, 1H), 5.29 (dd, J = 7.3 Hz, J = 8.5 Hz, 1H), 7.16 (d, J = 3.7 Hz, 2H), 7.19-7.23 (m, 2H), 7.27-7.33 (m, 12H), 7.49 (d, J = 3.8 Hz, 2H), 7.59 (d, J = 3.8 Hz, 2H); ^{13}C NMR $\{^1\text{H}\}$ (125 MHz CDCl_3) δ 38.0, 51.1, 67.4, 70.3, 72.8, 78.8, 126.0, 126.7, 127.0, 127.1,

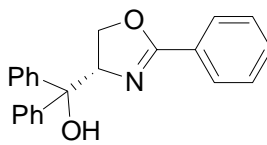
127.4, 128.38, 128.44, 128.6, 128.7, 129.0, 129.4, 136.07, 136.11, 144.2, 146.3, 156.7, 169.0; HRMS (CI, isobutane) m/z (M+H)⁺ calcd. 507.2284, obsd. 507.2274.



(1d): Yield: 76%; White solid; mp: 63-66 °C; $[\alpha]_D^{20} = -31.5^\circ$ (c = 0.33, CHCl₃); IR (KBr) 3416, 3340, 3060, 3029, 1702, 1663, 1496, 1449, 1248, cm⁻¹; ¹H NMR (500 MHz CDCl₃) δ 2.19 (s, 1H), 3.06 (dd, $J = 5.6$ Hz, $J = 13.7$ Hz, 1H), 3.22 (dd, $J = 5.2$ Hz, $J = 13.8$ Hz, 1H), 4.15 (dd, $J = 9.3$ Hz, $J = 9.3$ Hz, 1H), 4.21 (dd, $J = 8.7$ Hz, $J = 8.7$ Hz, 1H), 4.67-4.71 (m, 1H), 5.11 (s, 2H), 5.29 (dd, $J = 9.3$ Hz, $J = 9.3$ Hz, 1H), 5.34 (d, $J = 3.2$ Hz, 1H), 7.11-7.12 (m, 2H), 7.19-7.37 (m, 14H), 7.41-7.42 (m, 2H), 7.49 (d, $J = 3.8$ Hz, 2H); ¹³C NMR {¹H} (125 MHz CDCl₃) δ 37.8, 51.0, 67.2, 70.2, 72.7, 77.9, 125.8, 126.8, 127.1, 127.2, 127.35, 128.41, 128.43, 128.47, 128.6, 128.7, 128.8, 128.9, 136.0, 136.5, 144.1, 146.1, 155.8, 168.9; HRMS (CI, isobutane) m/z (M+H)⁺ calcd. 507.2284, obsd. 507.2307.

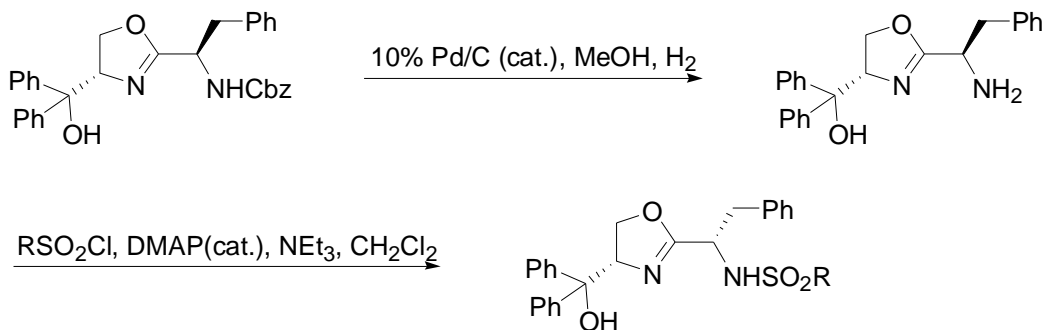


(10): Yield: 77%; White Solid; mp: 59 °C (glassy mass); $[\alpha]_D^{20} = -21.3^\circ$ (c = 0.4, CHCl₃); IR (KBr) 3423, 2964, 1708, 1663, 1509, 1449, 1230, 1215 cm⁻¹; ¹H NMR (500 MHz CDCl₃) δ 0.96 (d, $J = 3.4$ Hz, 3H), 1.01 (d, $J = 3.4$ Hz, 3H), 2.09-2.15 (m, 1H), 3.33 (s, 1H), 4.14 (dd, $J = 9.3$ Hz, $J = 9.3$ Hz, 1H), 4.20 (dd, $J = 5.6$ Hz, $J = 7.8$ Hz, 1H), 4.27 (dd, $J = 7.7$ Hz, $J = 7.7$ Hz, 1H), 4.71 (d, $J = 6$ Hz, 1H), 5.02 (d, $J = 6$ Hz, 1H), 5.15 (d, $J = 3.9$ Hz, 1H), 5.30 (dd, $J = 7.1$ Hz, $J = 9.5$ Hz, 1H), 7.18-7.22 (m, 2H), 7.25-7.34 (m, 9H), 7.48 (d, $J = 3.8$ Hz, 2H), 7.63 (d, $J = 3.9$ Hz, 2H); ¹³C NMR {¹H} (125 MHz CDCl₃) δ 18.2, 19.4, 30.7, 55.6, 67.4, 70.1, 72.6, 78.8, 126.0, 126.8, 127.0, 128.38, 128.42, 128.6, 128.7, 136.2, 144.3, 146.3, 157.3, 169.5; HRMS (CI, isobutane) m/z (M+H)⁺ calcd. 459.2284, obsd. 459.2305



(1e): Yield 56%; White solid; mp: 182-185 °C; $[\alpha]_D^{20} = -56.3^\circ$ (c = 0.16, CHCl₃); IR (KBr) 3538, 1645, 1493, 1450, 1357 cm⁻¹; ¹H NMR (500 MHz CDCl₃) δ 2.59 (m, 1H), 4.24-4.30 (m, 2H), 5.51 (dd, $J = 9.4$ Hz, $J = 9.4$ Hz, 1H), 7.21-7.41 (m, 8H), 7.47-7.50 (m, 3H), 7.68-7.70 (m, 2H), 7.94-7.96 (m, 2H); ¹³C NMR {¹H} (125 MHz CDCl₃) δ 69.5, 73.4, 78.5, 126.0, 127.1, 127.27, 127.31, 127.6, 128.4, 128.5, 128.6, 128.8, 131.9, 144.4, 146.3, 166.9; HRMS (CI, isobutane) m/z (M+H)⁺ calcd. 330.1494, obsd. 330.1496.

Synthesis of sulfonamides:



Deprotection:⁷

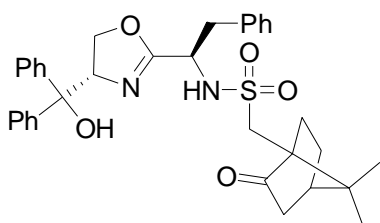
A Schlenk tube is charged with 144 mg of 10% Pd/C and the tube is flushed with argon. In a 100 mL flask, 1.433g of oxazoline **1g** (2.84 mmol) is dissolved in 20 mL of dry MeOH and cannulated in to the Schlenk tube (On occasions when this is difficult, gentle warming or addition of excess MeOH is helpful. Addition of excess MeOH has no discernible effect on overall yield). A further 5 mL is used for rinsing. The tube is then evacuated under aspirator pressure and filled with H₂ from a balloon. The cycle is repeated thrice more and the tube is left under an H₂ balloon. On completion of reaction (3.5-4h, by disappearance of oxazoline on TLC. 50% ethyl acetate in hexanes. oxazoline, R_f = 0.63), the reaction mixture is filtered through a pad of celite. The filtrate is concentrated and rotavaped with benzene (2 X 30 mL). The residue is dried overnight under high vacuum and used without further purification

Sulfonamidation:

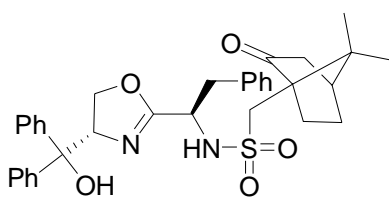
The residue from deprotection is dissolved in 15 mL of dry CH₂Cl₂ under argon along with 35 mg of DMAP (0.28 mmol, 10 mol%). To this solution 1.6 mL of freshly distilled triethylamine is added. In a separate flask, 735 mg of (*S*)-10-camphorsulfonyl chloride (2.84 mmol) is dissolved in 7 mL CH₂Cl₂ and cannulated into the flask containing the amine. A further 3 mL of CH₂Cl₂ is used for rinsing. On completion, the reaction mixture is diluted with 40 mL of CH₂Cl₂ and extracted with saturated aqueous NaHCO₃ (2 X 40 mL). The organic layer is dried over Na₂SO₄ and concentrated.

Column chromatography:

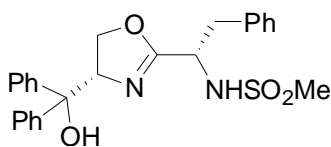
Approximately, 100 mL of SiO₂ is packed into a column with a 1:1 mixture of ether and hexanes as the solvent. The residue from work up is dissolved in minimum amount of CH₂Cl₂ and loaded on to the column. After an initial elution of 12 fractions (16 X 125 test tubes) with a 1:1 mixture of ether and hexanes as the solvent, the eluting solvent is switched to a 2:1 mixture of ether and hexanes. Fractions 12-24 were concentrated to yield 1.909g of the oxazoline sulfonamide as a white solid (55%, Average 57%)



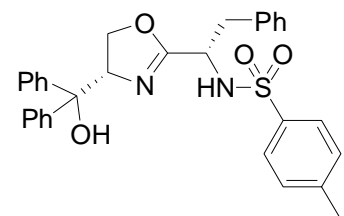
(II): mp: 92 °C (dec); [α]_D²⁰ = 5.4° (c = 0.26, CHCl₃); IR (KBr) 3483, 3473, 2960, 1738, 1666, 1449, 1328, 1147, cm⁻¹; ¹H NMR (500 MHz CDCl₃) δ 0.62 (s, 3H), 0.98 (s, 3H), 1.28 (ddd, *J* = 3.8 Hz, *J* = 9.4 Hz, *J* = 12.8 Hz, 1H), 1.50 (ddd, *J* = 4.6 Hz, *J* = 9.3 Hz, *J* = 14.1 Hz, 1H), 1.76 (d, *J* = 9.3 Hz, 1H), 1.91 (dddd *J* = 3.2 Hz, *J* = 7.6 Hz, *J* = 11.7 Hz, *J* = 15.1 Hz, 1H), 1.96 (dd, *J* = 4.4 Hz, *J* = 4.4 Hz, 1H), 2.09 (ddd, *J* = 3.8 Hz, *J* = 3.8 Hz, *J* = 18.6 Hz, 1H), 2.18 (ddd, *J* = 3.8 Hz, *J* = 11.6 Hz, *J* = 14.8 Hz, 1H), 2.77 (d, *J* = 7.7 Hz, 1H), 3.08 (dd, *J* = 6.5 Hz, *J* = 13.8 Hz, 1H), 3.16 (dd, *J* = 5.6 Hz, *J* = 13.7 Hz, 1H), 3.27 (d, *J* = 7.6 Hz, 1H), 3.54 (s, 1H), 4.13 (dd, *J* = 8.7 Hz, *J* = 9.9 Hz, 1H), 4.31 (dd, *J* = 7.6 Hz, *J* = 8.5 Hz, 1H), 4.52 (m 1H), 5.19 (dd, *J* = 7.6 Hz, *J* = 9.8 Hz, 1H), 5.37 (d, *J* = 4.3 Hz, 1H), 7.12-7.15 (m, 1H), 7.16-7.19 (m, 1H), 7.21-7.30 (m, 9H), 7.41-7.43 (m, 2H), 7.51-7.53 (m, 2H); ¹³C NMR {¹H} (125 MHz CDCl₃) δ 19.9, 20.0, 26.6, 26.9, 39.8, 42.7, 43.3, 48.2, 51.0, 52.7, 59.1, 70.6, 72.8, 78.6, 126.0, 127.0, 127.1, 127.2, 12.4, 128.2, 128.5, 128.8, 129.9, 135.9, 144.7, 146.0, 169.0, 216.6; HRMS (CI, isobutane) *m/z* (M+H)⁺ calcd. 587.2579, obsd. 587.2567.



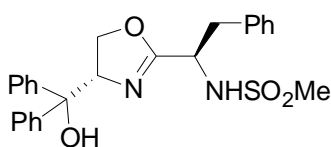
(1j): Yield:60%; White solid; mp: 126 °C (dec); $[\alpha]_D^{20} = -45.5^\circ$ ($c = 0.11$, CHCl_3); IR (KBr) 3461, 3449, 2960, 1736, 1664, 1449, 1365, 1341, 1325, 1148, 702, cm^{-1} ; ^1H NMR (500 MHz CDCl_3) δ 0.73 (s, 3H), 0.85-0.9 (m, 1H), 0.93 (s, 3H), 1.2-1.28 (m, 2H) 1.79 (dddd $J = 4.4$ Hz, $J = 7.8$ Hz, $J = 12.2$ Hz, $J = 16.4$ Hz, 1H), 1.92 (dd, $J = 4.4$ Hz, $J = 4.4$ Hz, 1H), 2.01 (ddd, $J = 4.2$ Hz, $J = 4.2$ Hz, $J = 18.8$ Hz, 1H), 2.24-2.30 (m, 1H), 2.79 (d, $J = 7.6$ Hz, 1H), 3.19 (dd, $J = 4.2$ Hz, $J = 13.7$ Hz, 1H), 3.33(dd, $J = 5.5$ Hz, $J = 13.7$ Hz, 1H), 3.47 (d, $J = 7.7$ Hz, 1H), 3.96 (s, 1H), 4.10 (dd, $J = 8.7$ Hz, $J = 9.8$ Hz, 1H), 4.42 (dd, $J = 7$ Hz, $J = 8.4$ Hz, 1H), 4.64 (dd, $J = 4.9$ Hz, $J = 4.9$ Hz, 1H), 5.04 (dd, $J = 6.9$ Hz, $J = 10$ Hz, 1H), 5.34 (brs 1H), 7.15-7.19 (m, 2H), 7.22-7.32 (m, 9H), 7.38-7.4 (m, 2H), 7.52-7.54 (m, 2H); ^{13}C NMR $\{^1\text{H}\}$ (125 MHz CDCl_3) δ 19.5, 19.8, 24.3, 26.6, 39.5, 42.1, 42.4, 48.77, 48.84, 53.0, 58.4, 70.6, 72.4, 78.4, 126.0, 126.9, 127.08, 127.10, 127.8, 128.1, 128.47, 128.48, 130.5, 135.9, 144.7, 146.3, 168.1, 218.3; HRMS (CI, isobutane) m/z (M+H) $^+$ calcd. 587.2579, obsd. 587.2594.



(1b): Yield:59%; Light yellow solid; mp: 145 °C (dec); $[\alpha]_D^{20} = -33.9^\circ$ ($c = 0.24$, CHCl_3); IR (KBr) 3475, 3297, 16732, 1450, 1353, 1326, 1145, 1114, cm^{-1} ; ^1H NMR (500 MHz CDCl_3) δ 2.20 (s, 1H), 2.74 (s, 3H), 3.02, (dd, $J = 7$ Hz, $J = 13.8$ Hz, 1H), 3.15 (dd, $J = 5.2$ Hz, $J = 13.8$ Hz, 1H), 4.2 (dd, $J = 8.8$ Hz, $J = 9.9$ Hz, 1H), 4.28 (dd, $J = 8.8$ Hz, $J = 8.8$ Hz, 1H), 4.45-4.49 (m, 1H), 4.86 (d, $J = 3.9$ Hz, 1H), 5.32 (ddd, $J = 1.2$ Hz, $J = 8.8$ Hz, $J = 10$ Hz, 1H), 7.19-7.24, (m, 4H), 7.29-7.36 (m, 7H), 7.40-7.43 (m 2H), 7.48-7.50 (m 2H); ^{13}C NMR $\{^1\text{H}\}$ (125 MHz CDCl_3) δ 39.6, 41.3, 53.2, 70.6, 72.7, 78.0, 125.8, 126.8, 127.3, 127.4, 127.7, 128.5, 128.6, 129.0, 130.0, 135.6, 144.0, 145.9, 168.8; HRMS (CI, isobutane) m/z (M+H) $^+$ calcd. 451.1692, obsd. 451.1701.

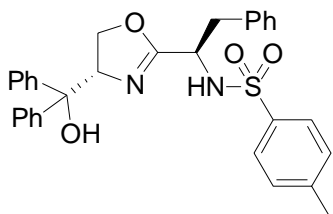


(1c): Yield 66%; White solid; mp: 81-83 °C (glassy mass); $[\alpha]_D^{20} = -147.9^\circ$ ($c = 0.31$, CHCl_3); IR (KBr) 3449, 1664, 1449, 1340, 1331, 1161, 1092, 701, cm^{-1} ; ^1H NMR (500 MHz CDCl_3) δ 2.24 (s, 1H), 2.44 (s, 3H), 2.98 (dd, $J = 6.7$ Hz, $J = 13.8$ Hz, 1H), 3.07 (dd, $J = 5.4$ Hz, $J = 13.8$ Hz, 1H), 4.03, (dd, $J = 8.7$ Hz, $J = 9.8$ Hz, 1H), 4.15 (dd, $J = 8.8$ Hz, $J = 8.8$ Hz, 1H), 4.21 (dd, $J = 6.4$ Hz, $J = 6.4$ Hz, 1H), 5.01-5.07 (m, 2H), 7.05-7.07 (m, 2H), 7.18-7.33(m, 11H), 7.37-7.39 (m, 2H), 7.43-7.44 (m, 2H), 7.58 (d, $J = 4.2$ Hz, 2H); ^{13}C NMR $\{^1\text{H}\}$ (125 MHz CDCl_3) δ 21.8, 39.1, 52.5, 70.4, 72.7, 77.9, 125.7, 126.7, 127.2, 127.3, 127.5, 127.7, 128.4, 128.6, 128.9, 129.7, 129.8, 135.1, 136.4, 143.8, 144.0, 146.0, 168.2; HRMS (CI, isobutane) m/z (M+H) $^+$ calcd. 527.2005; obsd. 527.2016.

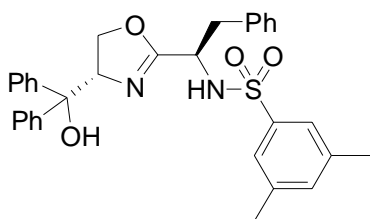


(1a): Yield:57%; Light yellow solid; mp: 135 °C (dec); $[\alpha]_D^{20} = -6.1^\circ$ ($c = 0.23$, CHCl_3), IR (KBr) 3461, 1662, 1449, 1314, 1149, 980, cm^{-1} ; ^1H NMR (500 MHz CDCl_3) δ 2.56 (s, 3H), 2.88(s, 1H), 2.92 (dd, $J = 8.8$ Hz, $J = 13.9$ Hz, 1H), 3.18 (dd, $J = 5.1$ Hz, $J = 13.7$ Hz, 1H), 4.22 (dd, $J = 8.7$ Hz, $J = 9.6$ Hz,

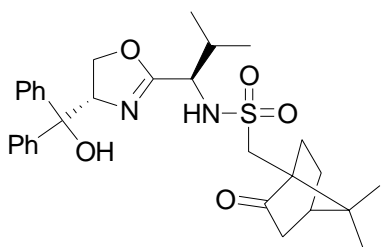
1H), 4.32 (dd, $J = 7.3$ Hz, $J = 8.8$ Hz, 1H), 4.40 (ddd, $J = 5.3$ Hz, $J = 8.3$ Hz, $J = 8.3$ Hz, 1H), 4.73 (d, $J = 3.8$ Hz, 1H), 5.31 (dd, $J = 7.3$ Hz, $J = 9.8$ Hz, 1H), 7.19-7.23 (m, 4H), 7.27-7.35 (m, 7H), 7.45-7.48 (m, 2H), 7.54-7.56 (m, 2H); ^{13}C NMR $\{^1\text{H}\}$ (125 MHz CDCl_3) δ 39.5, 41.5, 53.4, 70.5, 73.2, 78.8, 125.9, 126.6, 127.2, 127.3, 127.7, 128.5, 128.7, 129.1, 129.6, 135.8, 144.0, 145.9, 169.1; HRMS (CI, isobutane) m/z ($\text{M}+\text{H}$) $^+$ calcd. 451.1692, obsd. 451.1700.



(1h): Yield: 52% ; White solid; mp: 81 °C (glassy mass); $[\alpha]_{\text{D}}^{20} = 9.6^\circ$ ($c = 0.24$, CHCl_3), IR (KBr) 3547, 3483, 3291, 1664, 1449, 1356, 1340, 1162 cm^{-1} ; ^1H NMR (500 MHz CDCl_3) δ 1.77 (s, 1H), 2.39 (s, 3H), 3.01 (dd, $J = 6.4$ Hz, $J = 13.8$ Hz, 1H), 3.07 (dd, $J = 5.6$ Hz, $J = 13.8$ Hz, 1H), 4.01 (dd, $J = 8.8$ Hz, $J = 9.8$ Hz, 1H), 4.11 (dd, $J = 8.2$ Hz, $J = 8.2$ Hz, 1H), 4.21 (ddd, $J = 6$ Hz, $J = 6$ Hz, $J = 9.0$ Hz, 1H), 5.00 (dd, $J = 7.9$ Hz, $J = 9.9$ Hz, 1H), 5.15 (d, $J = 4.4$ Hz, 1H), 7.01 (d, $J = 4.0$ Hz, 2H), 7.11-7.13 (m, 2H), 7.17-7.33 (m, 11H), 7.41-7.43 (m, 2H), 7.5-7.52 (m, 2H); ^{13}C NMR $\{^1\text{H}\}$ (125 MHz CDCl_3) δ 21.8, 39.9, 52.4, 70.7, 72.5, 78.2, 125.8, 127.0, 127.1, 127.3, 127.4, 127.6, 128.3, 128.5, 128.7, 129.7, 129.9, 135.5, 136.4, 143.8, 144.1, 145.6, 168.5; HRMS (CI, isobutane) m/z ($\text{M}+\text{H}$) $^+$ calcd. 527.2005; obsd. 527.1996.

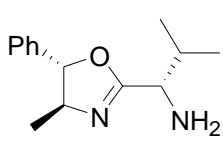


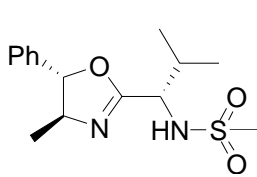
(1i): Yield 51%, White solid; mp: 81-85 °C (glassy mass); $[\alpha]_{\text{D}}^{20} = 21.3^\circ$ ($c = 0.23$, CHCl_3), IR (KBr) 3483, 3298, 1665, 1449, 1364, 1339, 1304, 1156 cm^{-1} ; ^1H NMR (500 MHz CDCl_3) δ 2.27 (s, 6H), 2.96 (dd, $J = 7.2$ Hz, $J = 13.8$ Hz, 1H), 3.05 (dd, $J = 5.7$ Hz, $J = 13.8$ Hz, 1H), 4.03 (dd, $J = 9.3$ Hz, $J = 9.3$ Hz, 1H), 4.13 (dd, $J = 8.3$ Hz, $J = 8.3$ Hz, 1H), 4.18-4.22 (m, 1H), 5.07 (dd, $J = 9.6$ Hz, $J = 8.2$ Hz, 1H), 5.11-5.13 (m, 1H), 7.07-7.09 (m, 2H), 7.15-7.31 (m, 12H), 7.36-7.37 (m, 2H), 7.42-7.43 (m, 2H); ^{13}C NMR $\{^1\text{H}\}$ (125 MHz CDCl_3) δ 21.4, 39.8, 52.6, 70.6, 72.8, 78.3, 125.0, 125.9, 126.7, 127.2, 127.3, 127.4, 128.4, 128.6, 128.7, 129.7, 134.8, 135.5, 139.3, 144.1, 145.7, 168.8; HRMS (CI, isobutane) m/z ($\text{M}+\text{H}$) $^+$ calcd. 541.2161, obsd. 541.2160.



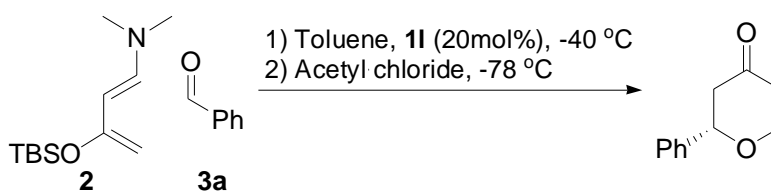
(1k): Yield: 79%; White solid; mp: 134-135 °C; $[\alpha]_{\text{D}}^{20} = 2.2^\circ$ ($c = 0.46$, CHCl_3); IR (KBr) 3534, 3311, 2964, 2930, 1724, 1670, 1447, 1361, 1335, 1201, 1164, 1133, 1053, 992, 701 cm^{-1} ; ^1H NMR (500 MHz CDCl_3) δ 0.67 (s, 3H), 0.93 (d, $J = 3.4$ Hz, 3H), 1.04 (s, 3H), 1.05 (d, $J = 3.4$ Hz, 3H), 1.21-1.28 (m, 1H), 1.37-1.44 (m, 1H), 1.82 (d, $J = 9.8$ Hz, 1H), 1.92 (dddd, $J = 4.4$ Hz, $J = 7.6$ Hz, $J = 12.2$ Hz, $J = 16.6$ Hz, 1H), 2.01 (dd, $J = 4.5$ Hz, $J = 4.5$ Hz, 1H), 2.18 (dddd, $J = 4.3$ Hz, $J = 6.8$ Hz, $J = 11$ Hz, $J = 13.7$ Hz, 1H), 2.23-2.29 (m, 2H), 2.76 (d, $J = 7.7$ Hz, 1H), 3.38 (d, $J = 7.6$ Hz, 1H), 3.75 (s, 1H), 4.06 (dd, $J = 4.3$ Hz, $J = 9.6$ Hz, 1H), 4.13 (dd, $J = 8.8$ Hz, $J = 9.8$ Hz, 1H), 4.32 (dd, $J = 8.1$ Hz, $J = 8.1$ Hz, 1H), 5.29 (dd, $J = 7.7$ Hz, $J = 9.9$ Hz, 1H), 5.80 (d, $J = 4.9$ Hz, 1H), 7.14-7.2 (m, 2H), 7.25-7.30 (m, 4H), 7.45-7.46 (m, 2H), 7.62-7.64 (m, 2H); ^{13}C NMR $\{^1\text{H}\}$ (125 MHz CDCl_3) δ 17.1, 19.3, 19.9, 20.1, 25.8, 26.9, 31.4, 42.6, 43.1, 48.3, 50.9, 56.1, 59.3, 70.7,

72.4, 78.6, 126.0, 126.9, 127.1, 127.5, 128.2, 128.5, 144.9, 146.1, 169.6, 217.2; HRMS (CI, isobutane) m/z (M+H)⁺ calcd. 539.2580, obsd. 539.2561.

 **(11):** Two step procedure for the synthesis of this compound is provided in reference 4. Two step yield from Fmoc (L)-valine: 79%; Light yellow oil; ¹H NMR (500 MHz CDCl₃) δ 1.01 (d, *J* = 3.4 Hz, 3H), 1.04 (d, *J* = 3.4 Hz, 3H), 1.40 (d, *J* = 3.3 Hz, 3H), 2.04-2.11 (m, 1H), 3.42 (d, *J* = 2.8 Hz, 1H) 4.00-4.06 (m, 1H), 4.94 (d, *J* = 3.9 Hz, 1H), 7.28-7.4 (m 5H); ¹³C NMR {¹H} (125 MHz CDCl₃) δ 17.6, 19.8, 21.7, 32.1, 55.8, 70.4, 88.6, 125.8, 128.5, 129.0, 140.6, 169.1.

 **(1f):** Synthesized according to the above procedure. Yield: 98%; Light yellow solid; mp: 107-110 °C; [α]_D²⁰ = -65.7° (c = 0.48, CHCl₃); IR (KBr) 3150, 3071, 2972, 2931, 1664, 1462, 1345, 1317, 1159, 1134, 1048 cm⁻¹; ¹H NMR (500 MHz CDCl₃) δ 0.97 (d, *J* = 3.9 Hz, 3H), 1.09 (d, *J* = 3.4 Hz, 3H), 1.40 (d, *J* = 3.4 Hz, 3H), 2.18-2.27 (m, 1H), 2.98 (s, 3H), 4.04-4.11 (m, 2H), 5.00 (d, *J* = 4.9 Hz, 1H), 5.04 (d, *J* = 3.9 Hz, 1H), 7.25-7.26 (m, 2H), 7.34-7.42 (m, 3H); ¹³C NMR {¹H} (125 MHz CDCl₃) δ 17.1, 19.4, 21.7, 31.5, 41.2, 57.2, 70.0, 89.7, 125.8, 128.9, 129.2, 139.7, 165.4; HRMS (CI, isobutane) m/z (M+H)⁺ calcd. 311.1429, obsd. 311.1434.

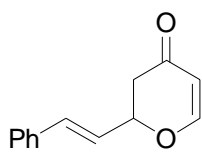
Hetero Diels-Alder Reaction:

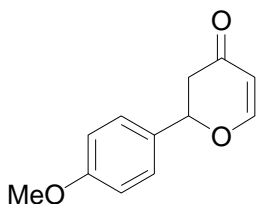


To a vial with a septum cap containing 70 mg of **11** under argon, 2 mL of toluene is added followed 122.5 μL of benzaldehyde. The vial is cooled to -55 °C and 136 mg of diene **2** dissolved in 0.5 mL of toluene is cannulated into it. A further 0.5 mL of toluene is used for rinsing. After stirring for two days at -55 °C, the reaction mixture is cooled to -78 °C, diluted with 2.5 mL of CH₂Cl₂, and 87.5 μL is added. After stirring for 45 min. the contents are directly transferred to column for chromatography:

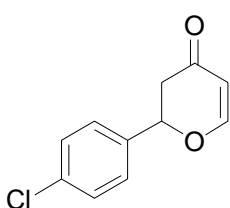
Column Chromatography:

Approximately, 50 mL of SiO₂ is packed into a column with 5% ethyl acetate in hexanes as the solvent. After an initial elution of 7 fractions (16 X 125 test tubes), the eluting solvent is switched to 15 % ethyl acetate in hexanes. Fractions 17-31 were concentrated to yield 64.5 mg of the pyranone as a yellow oil (62%). The enantiomeric excess was determined to be 90% by HPLC analysis (Chiralcel OD, Hexane/ ¹PrOH = 90/10, flow rate: 1 mL/min): *t*_{major} = 12.8 min (S), *t*_{minor} = 15.4 min (R)

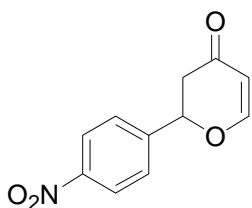
 Yield: 72%; light yellow solid. The enantiomeric excess was determined to be 88% by HPLC analysis (Chiralcel OD, Hexane/ ¹PrOH = 90/10, flow rate: 1 mL/min): *t*_{major} = 21.5 min (S), *t*_{minor} = 47.5 min (R)



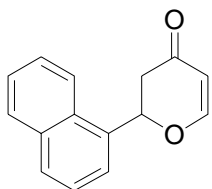
Yield 80%; Yellowish brown solid. The enantiomeric excess was determined to be 91% by HPLC analysis (Chiralcel OD, Hexane/ ⁱPrOH = 90/10, flow rate: 1 mL/min): $t_{\text{major}} = 16.7$ min, $t_{\text{minor}} = 18.9$ min.



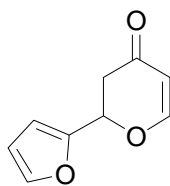
Yield 68%; yellow oil. The enantiomeric excess was determined to be 92% by HPLC analysis (Chiralcel OD, Hexane/ ⁱPrOH = 90/10, flow rate: 1 mL/min): $t_{\text{major}} = 13.5$ min, $t_{\text{minor}} = 16.8$ min.



Yield 62%; yellow solid. The enantiomeric excess was determined to be 88% by HPLC analysis (Chiralcel OD, Hexane/ ⁱPrOH = 90/10, flow rate: 1 mL/min): $t_{\text{major}} = 38.1$ min, $t_{\text{minor}} = 57.9$ min.



Yield 72%; yellow solid. The enantiomeric excess was determined to be 90% by HPLC analysis (Chiralpak AS, Hexane/ ⁱPrOH = 80/20, flow rate: 1 mL/min): $t_{\text{minor}} = 14.2$ min, $t_{\text{major}} = 22.4$ min.



Yield 42%; yellow solid. The enantiomeric excess was determined to be 71% by HPLC analysis (Chiralcel OD, Hexane/ ⁱPrOH = 90/10, flow rate: 0.5 mL/min): $t_{\text{minor}} = 24.1$ min, $t_{\text{major}} = 26$ min.

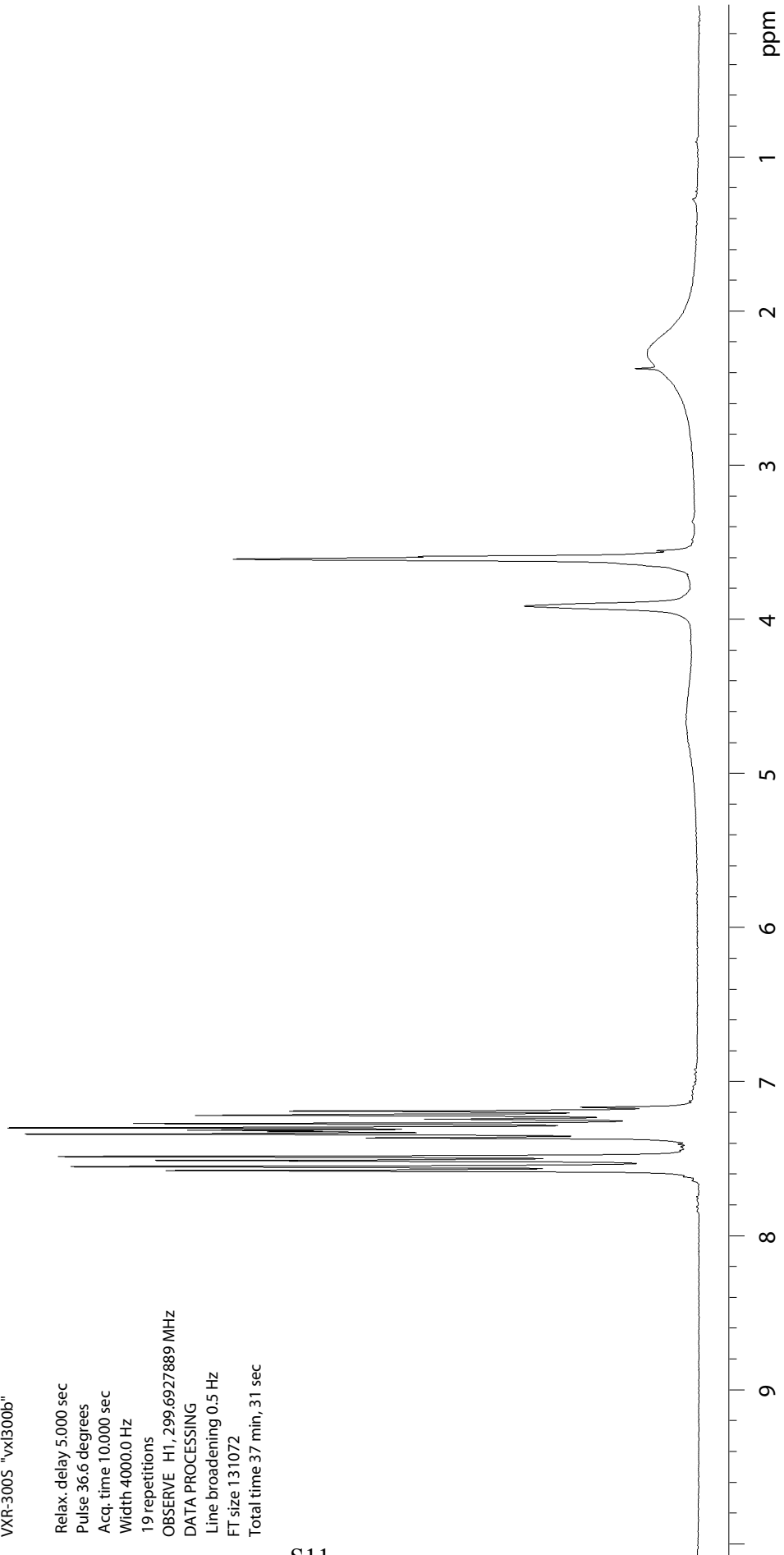
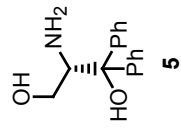
References:

- 1) Armarego, W. L. F.; Perrin, D. D. *Purification of Laboratory Chemicals*; Ed. 4.
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STANDARD 1H OBSERVE

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: n10p35
VXR-300S "vx1300b"

Relax. delay 5.000 sec
Pulse 36.6 degrees
Acq. time 10.000 sec
Width 4000.0 Hz
19 repetitions
OBSERVE H1, 299.6927889 MHz
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 37 min, 31 sec



¹³C OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl₃

Ambient temperature

File: n10p35c

UNITY-300 "unity300nmr"

Relax. delay 5.000 sec

Pulse 45.0 degrees

Acq. time 1.815 sec

Width 16501.7 Hz

870 repetitions

OBSERVE C13, 75.3577945 MHz

DECOUPLE H1, 299.6938675 MHz

Power 30 dB

continuously on

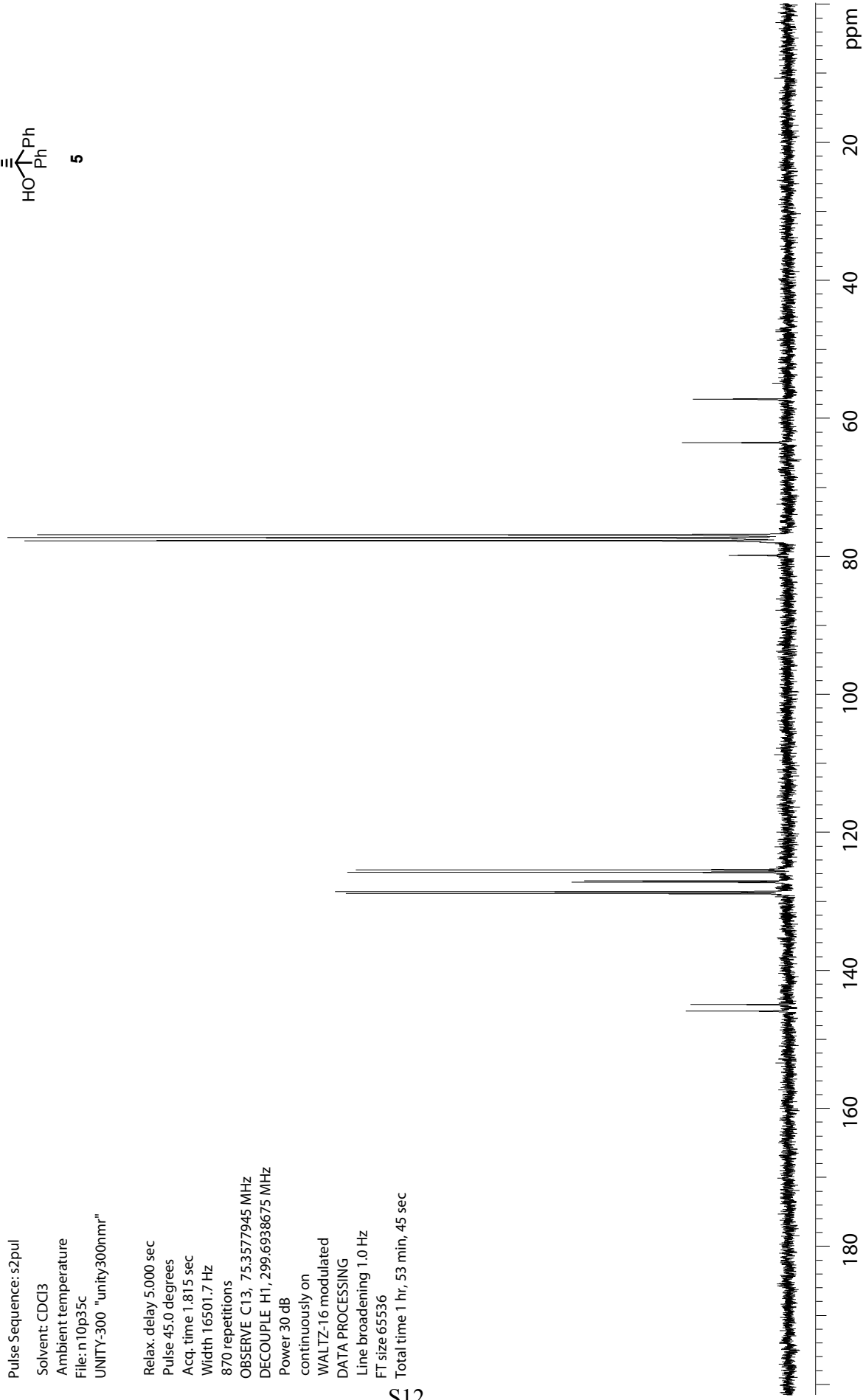
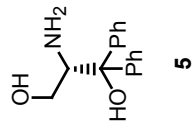
WALTZ-16 modulated

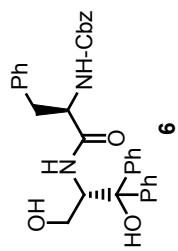
DATA PROCESSING

Line broadening 1.0 Hz

FT size 65536

Total time 1 hr, 53 min, 45 sec





STANDARD PROTON PARAMETERS

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

File: n10p121

VXR-300S "vx1300b"

Relax. delay 5.000 sec

Pulse 45.0 degrees

Acq. time 8.000 sec

Width 8000.0 Hz

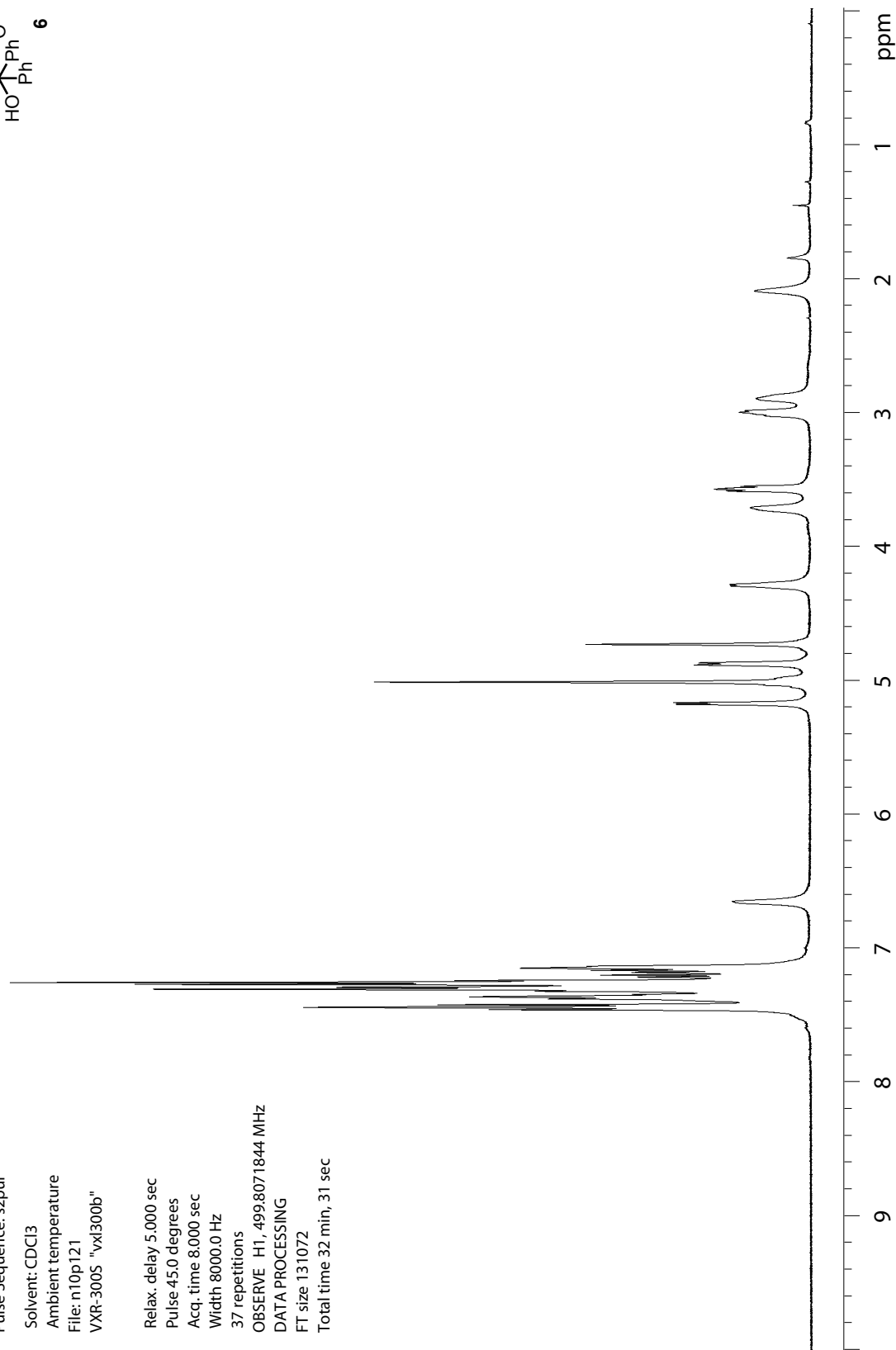
37 repetitions

OBSERVE H1, 499.8071844 MHz

DATA PROCESSING

FT size 131072

Total time 32 min, 31 sec



STANDARD CARBON PARAMETERS

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

User: 1-14-87

File: n10121c

UNITY-300 "unity300nmr"

Relax. delay 5.000 sec

Pulse 51.9 degrees

Acq. time 1.300 sec

Width 25000.0 Hz

480 repetitions

OBSERVE C13, 125.6765879 MHz

DECOUPLE H1, 499.8096844 MHz

Power 33 dB

continuously on

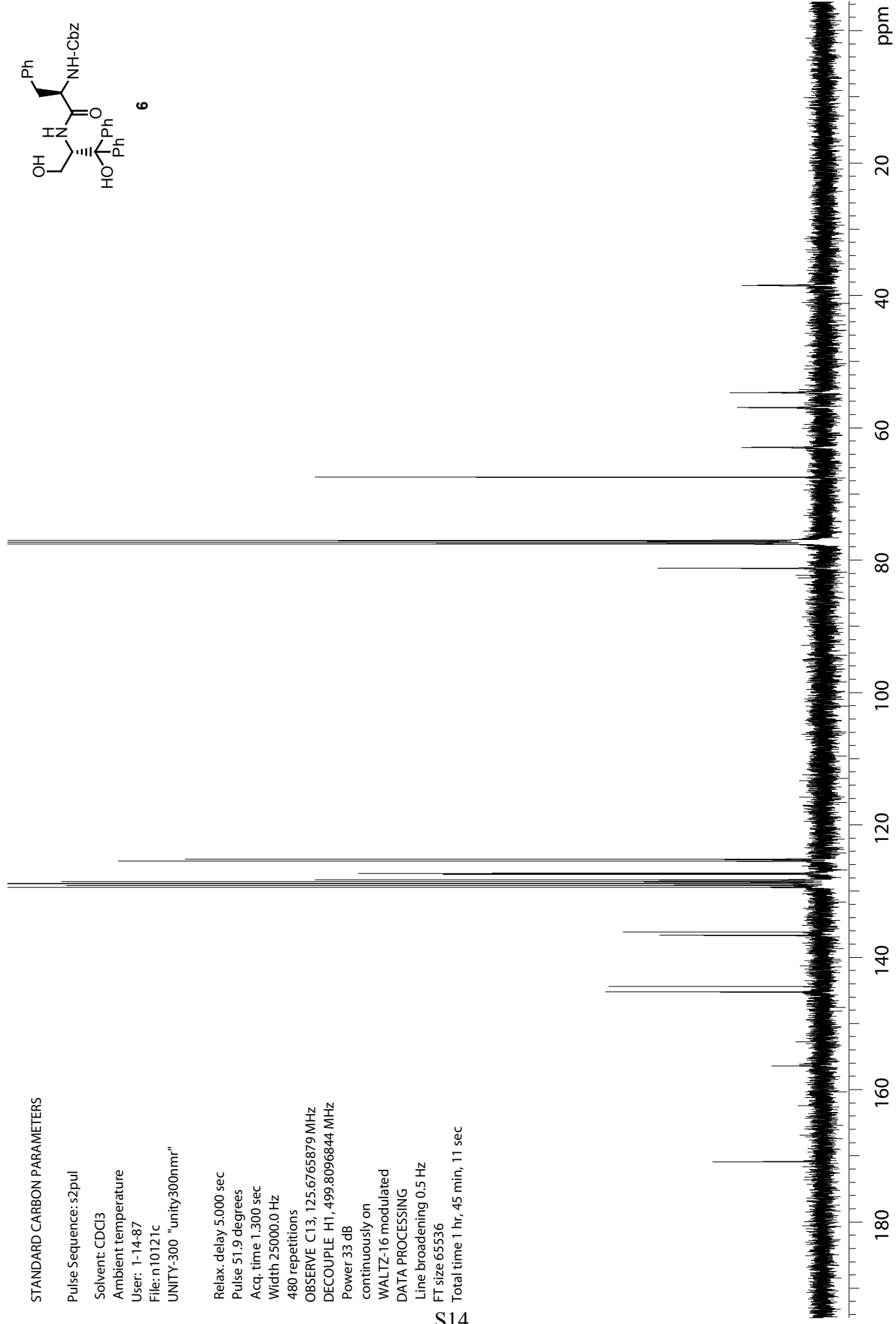
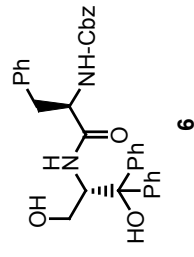
WALTZ-16 modulated

DATA PROCESSING

Line broadening 0.5 Hz

FT size 65536

Total time 1 hr, 45 min, 11 sec



STANDARD 1H OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl3

Temp: 40.0 C / 313.1 K

File: n9p113-40

VXR-300S "vx1300b"

Relax. delay 1.000 sec

Pulse 36.6 degrees

Acq. time 3.744 sec

Width 4000.0 Hz

20 repetitions

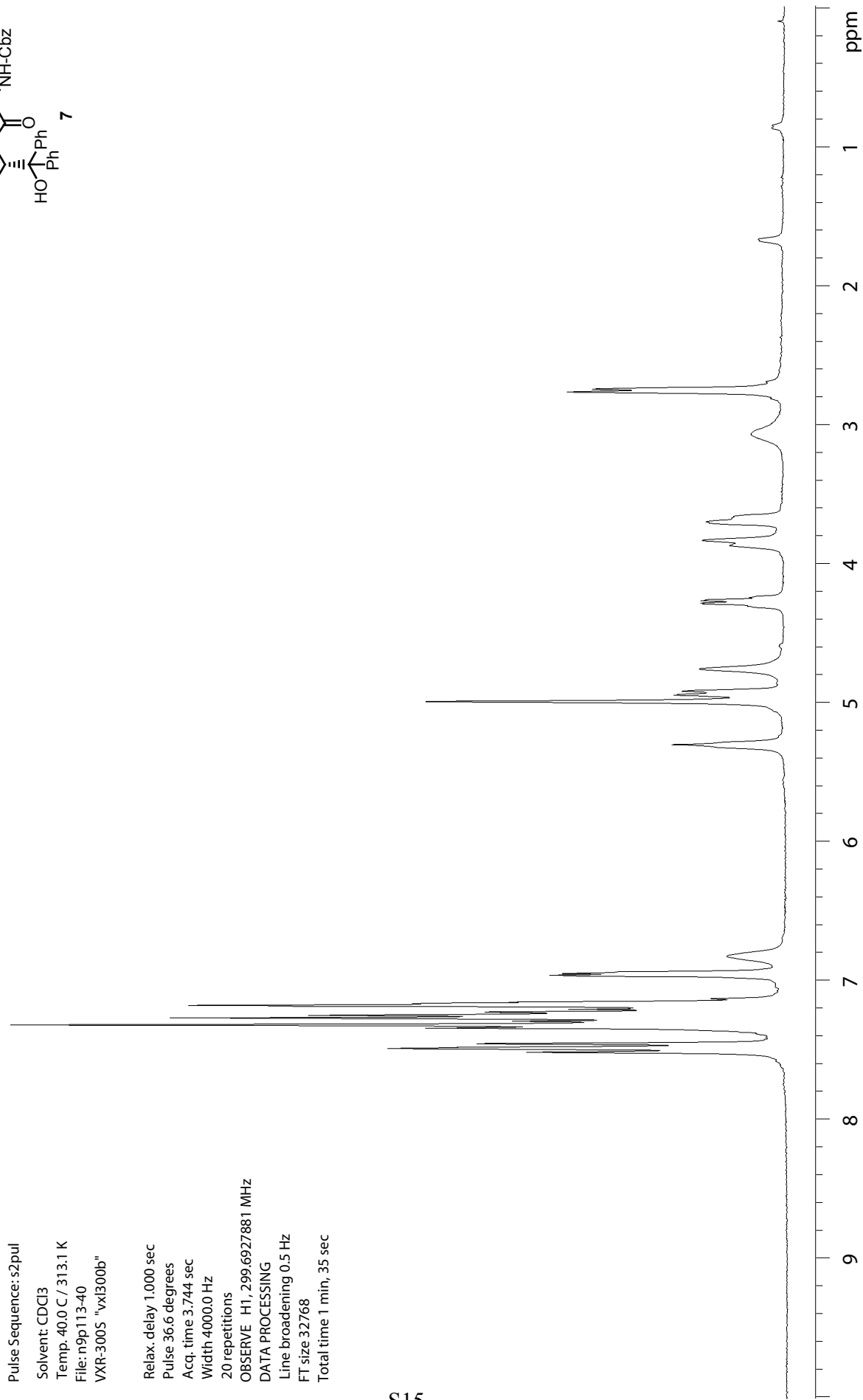
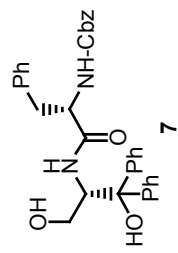
OBSERVE H1, 299.6927881 MHz

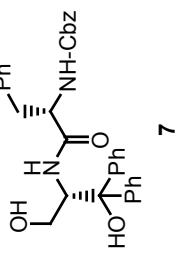
DATA PROCESSING

Line broadening 0.5 Hz

FT size 32768

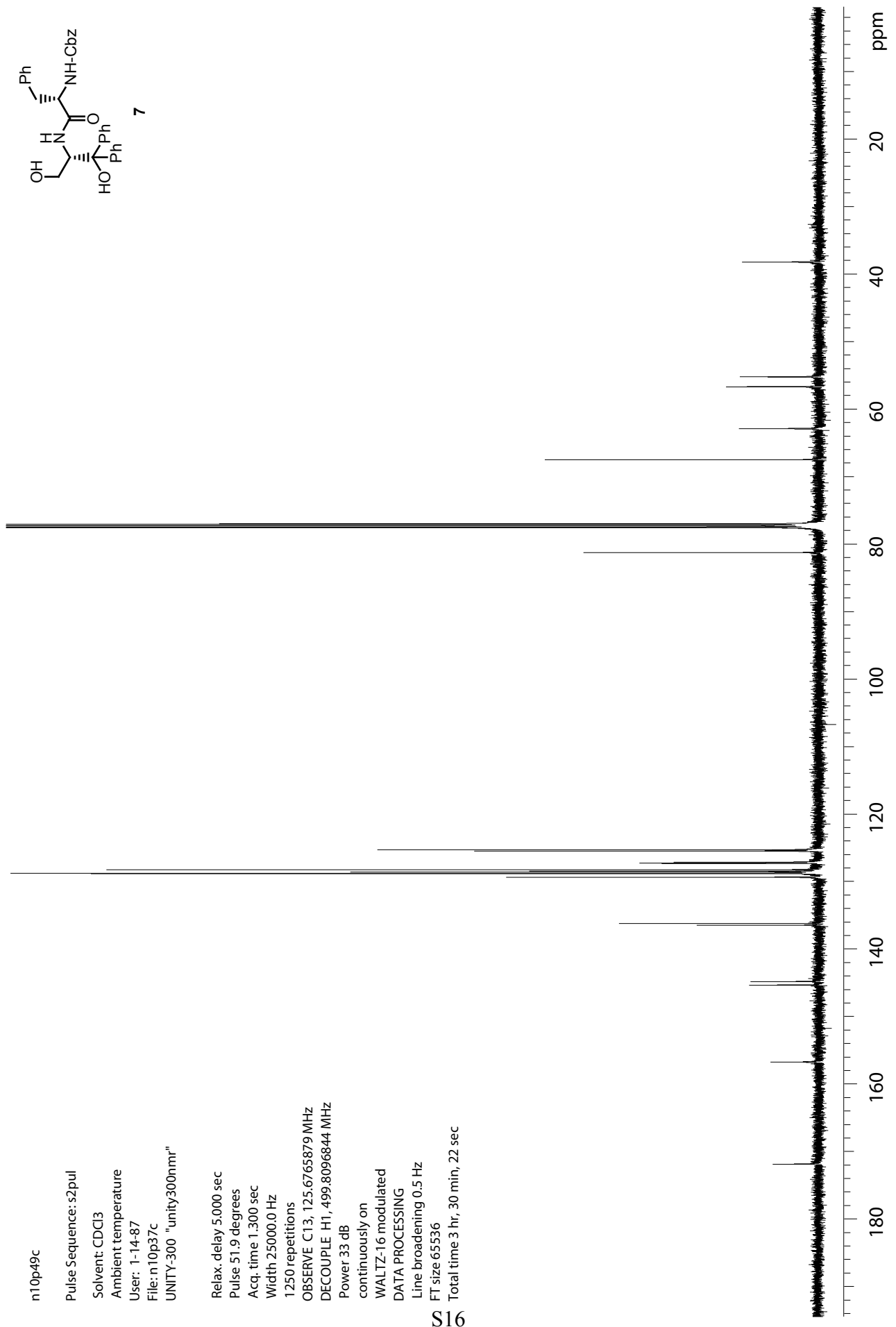
Total time 1 min, 35 sec





n10p49c
 Pulse Sequence: s2pul
 Solvent: CDCl3
 Ambient temperature
 User: 1-14-87
 File: n10p37c
 UNITY-300 "unity300nmr"

Relax. delay 5.000 sec
 Pulse 51.9 degrees
 Acq. time 1.300 sec
 Width 25000.0 Hz
 1250 repetitions
 OBSERVE C13, 125.6765879 MHz
 DECOUPLE H1, 499.8096844 MHz
 Power 33 dB
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 0.5 Hz
 FT size 65536
 Total time 3 hr, 30 min, 22 sec



STANDARD PROTON PARAMETERS

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

File: n9

VXR-300S "vx1300b"

Relax. delay 5.000 sec

Pulse 45.0 degrees

Acq. time 1.892 sec

Width 8000.0 Hz

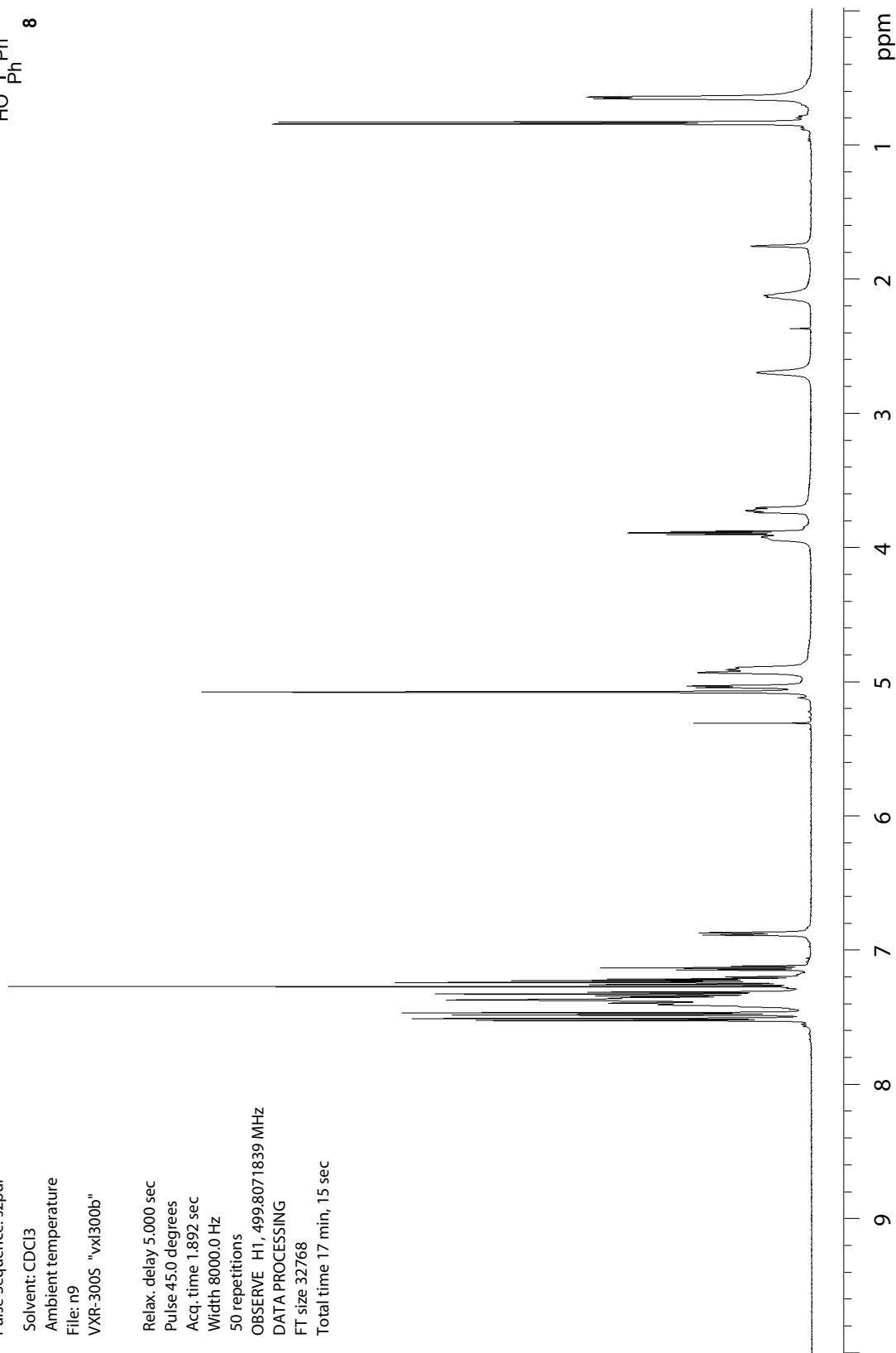
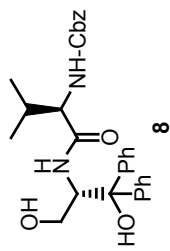
50 repetitions

OBSERVE H1, 499.8071839 MHz

DATA PROCESSING

FT size 32768

Total time 17 min, 15 sec



STANDARD CARBON PARAMETERS

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

User: 1-14-87

File: n9c

UNITY-500 "vyr500nm1"

Relax. delay 5.000 sec

Pulse 51.9 degrees

Acq. time 1.300 sec

Width 25000.0 Hz

860 repetitions

OBSERVE C13, 125.6765879 MHz

DECOUPLE H1, 499.8096844 MHz

Power 33 dB

continuously on

WALTZ-16 modulated

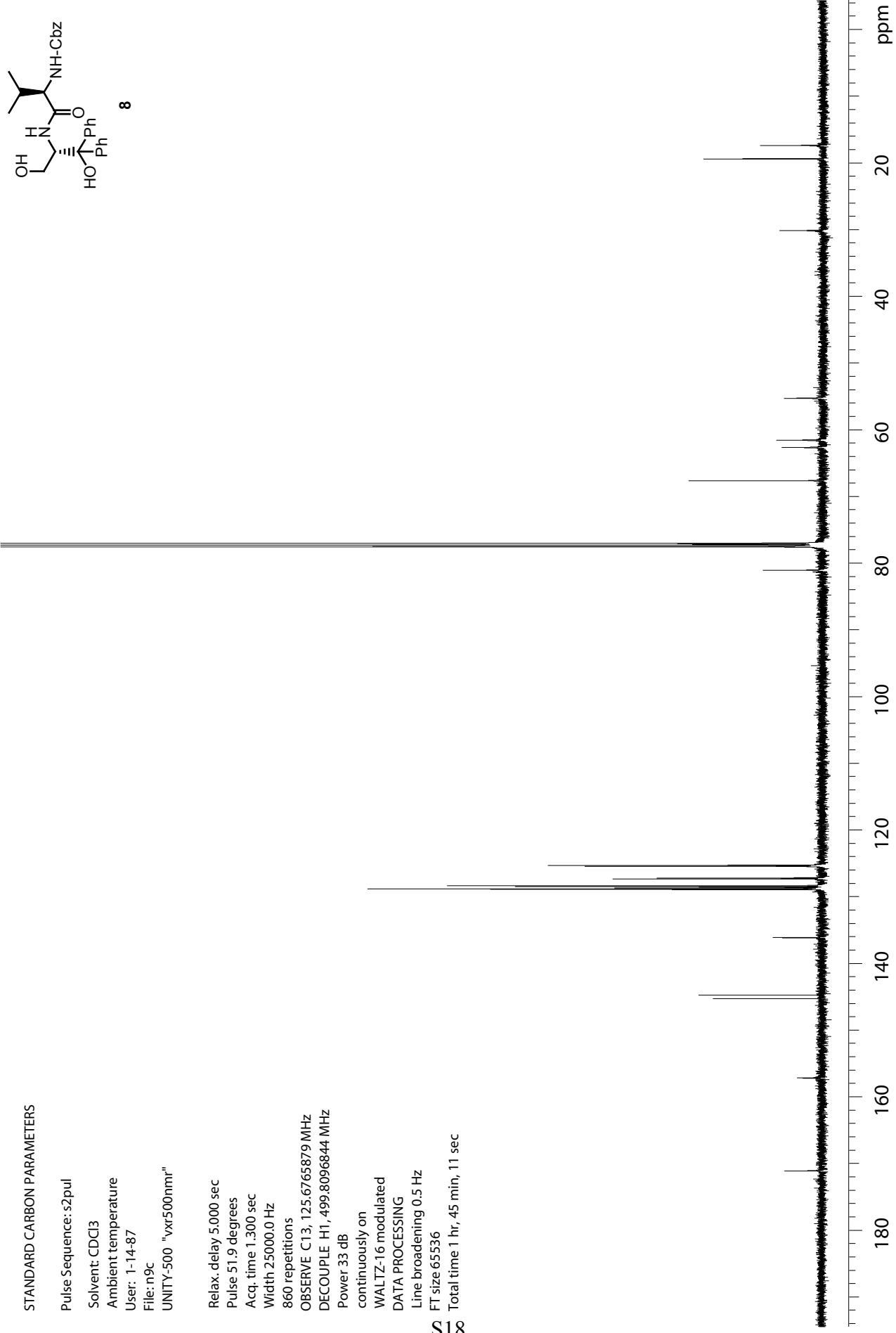
DATA PROCESSING

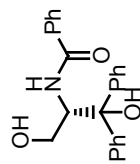
Line broadening 0.5 Hz

FT size 65536

Total time 1 hr, 45 min, 11 sec

8





9

STANDARD 1H OBSERVE

Pulse Sequence: s2pul

Solvent: CD3OD

Ambient temperature

File: n10p91

VXR-300S "vx1300b"

Relax. delay 5.000 sec

Pulse 36.6 degrees

Acq. time 10.000 sec

Width 4000.0 Hz

36 repetitions

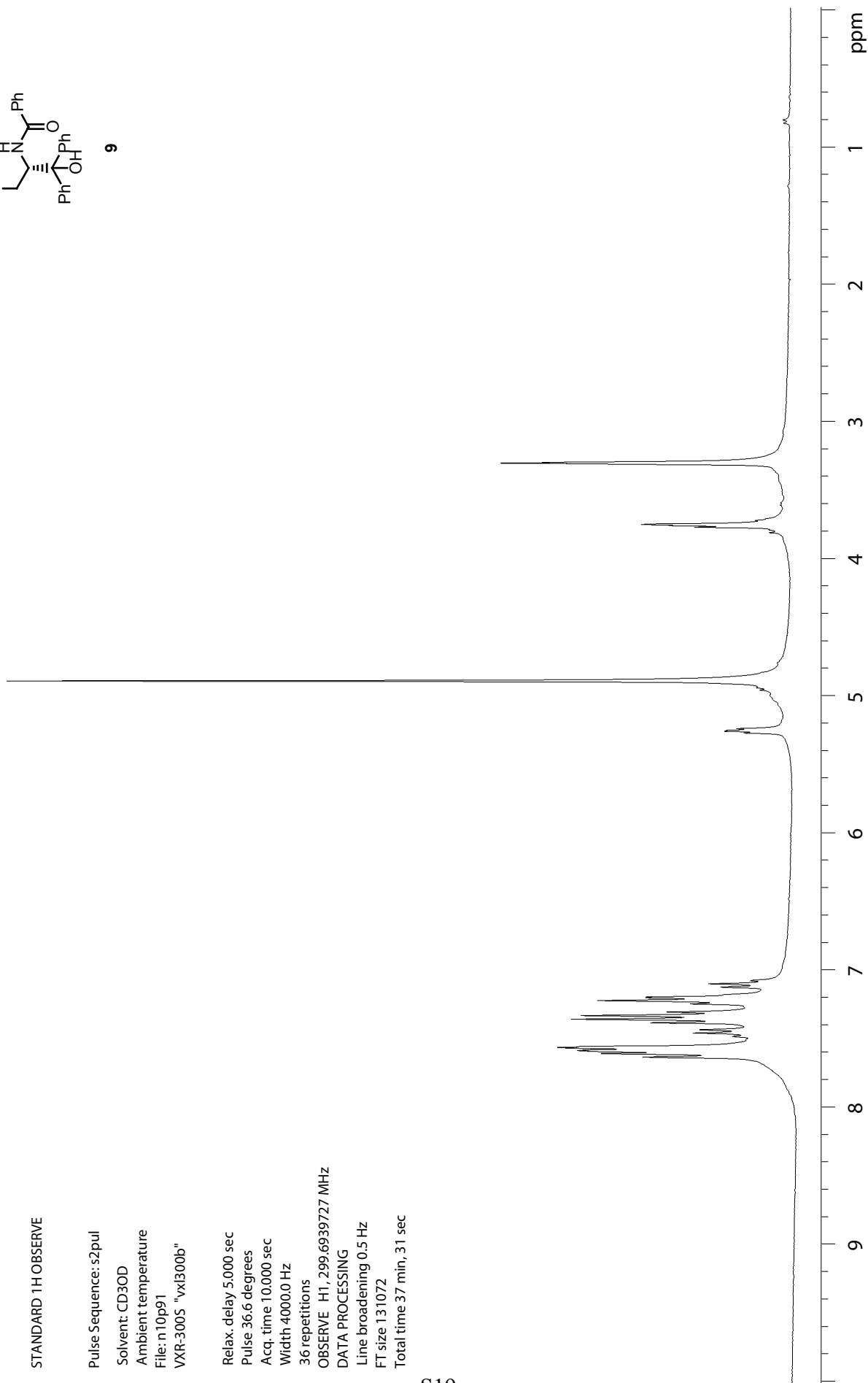
OBSERVE H1, 299.6939727 MHz

DATA PROCESSING

Line broadening 0.5 Hz

FT size 131072

Total time 37 min, 31 sec



¹³C OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl₃

Ambient temperature

File: n10p91c

UNITY-500 "vvr500nm1"

Relax. delay 5.000 sec

Pulse 45.0 degrees

Acq. time 1.815 sec

Width 16501.7 Hz

5790 repetitions

OBSERVE C13, 75.3577945 MHz

DECOUPLE H1, 299.6938675 MHz

Power 30 dB

continuously on

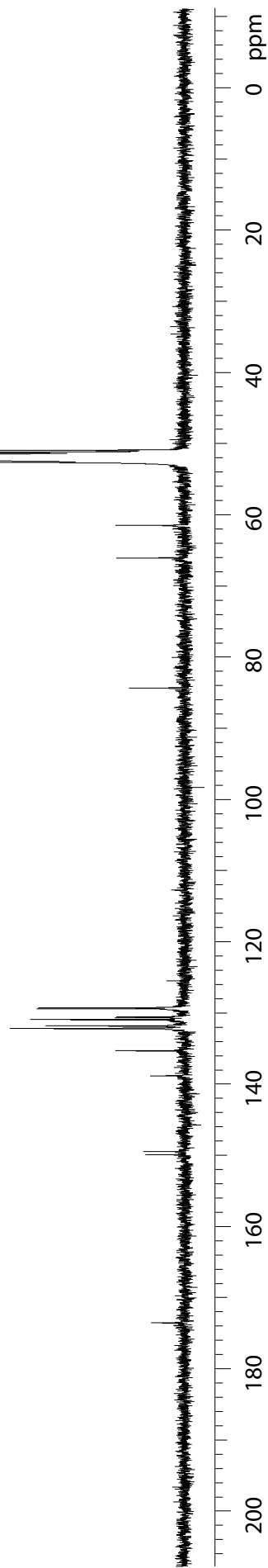
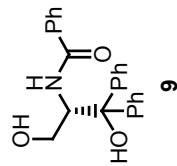
WALTZ-16 modulated

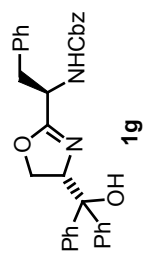
DATA PROCESSING

Line broadening 1.0 Hz

FT size 65536

Total time 18 hr, 57 min, 39 sec





n10p47

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

File: n10p47

VXR-300S "vx1300b"

Relax. delay 5.000 sec

Pulse 45.0 degrees

Acq. time 8.000 sec

Width 8000.0 Hz

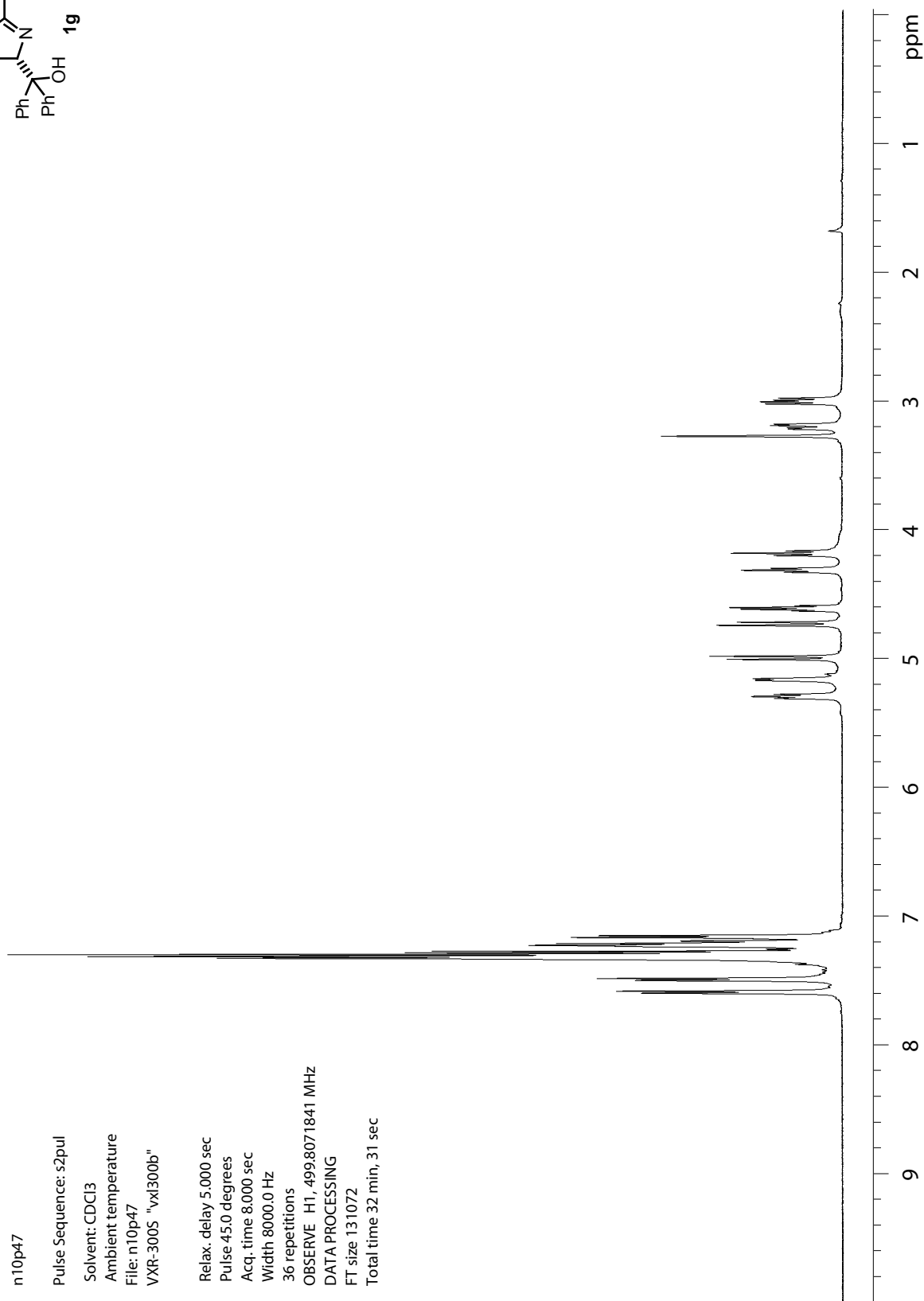
36 repetitions

OBSERVE H1, 499.8071841 MHz

DATA PROCESSING

FT size 131072

Total time 32 min, 31 sec



STANDARD CARBON PARAMETERS

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

User: 1-14-87

File: n10p47c

UNITY-300 "unity300nmr"

Relax. delay 5.000 sec

Pulse 51.9 degrees

Acq. time 1.300 sec

Width 25000.0 Hz

1310 repetitions

OBSERVE C13, 125.6765879 MHz

DECOUPLE H1, 499.8096844 MHz

Power 33 dB

continuously on

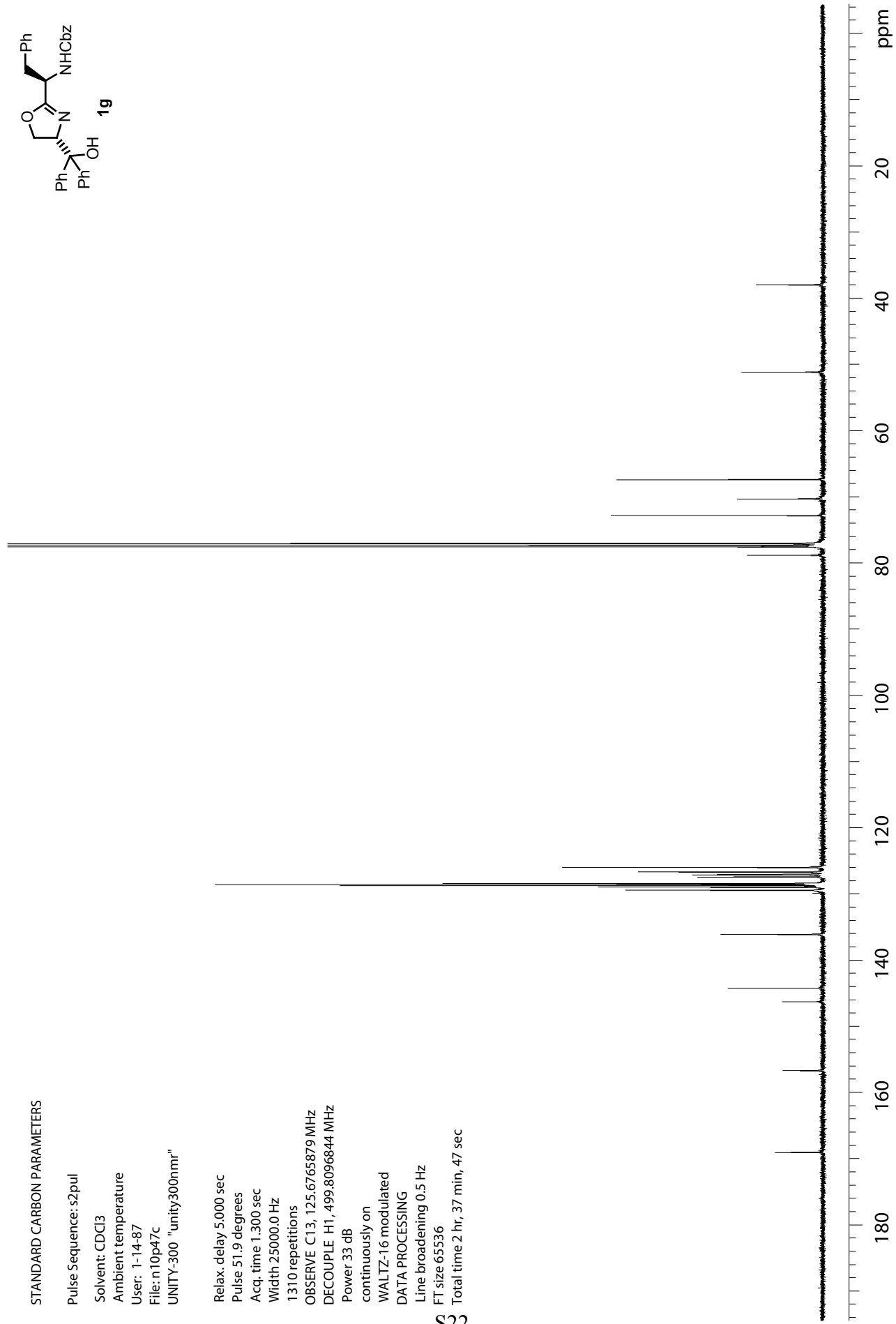
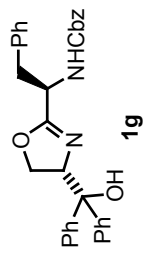
WALTZ-16 modulated

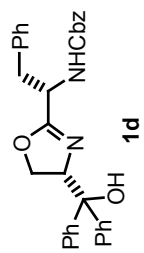
DATA PROCESSING

Line broadening 0.5 Hz

FT size 65536

Total time 2 hr, 37 min, 47 sec





STANDARD PROTON PARAMETERS

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

File: n9p119

VXR-300S "vx1300b"

Relax. delay 5.000 sec

Pulse 45.0 degrees

Acq. time 8.000 sec

Width 8000.0 Hz

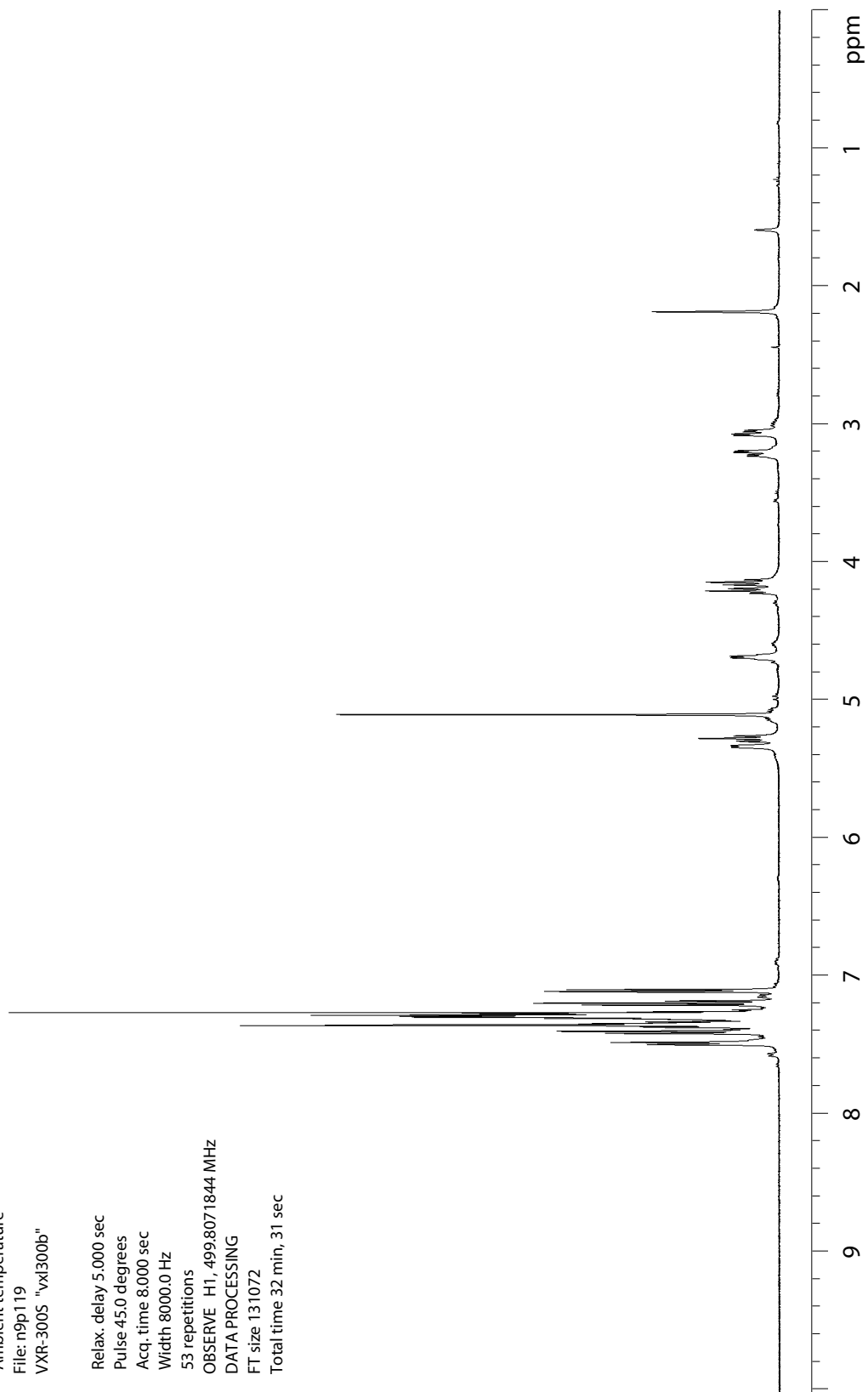
53 repetitions

OBSERVE H1, 499.8071844 MHz

DATA PROCESSING

FT size 131072

Total time 32 min, 31 sec



STANDARD PROTON PARAMETERS

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

File: n9p205

VXR-3005 "vxl300b"

Relax. delay 5.000 sec

Pulse 45.0 degrees

Acq. time 8.000 sec

Width 8000.0 Hz

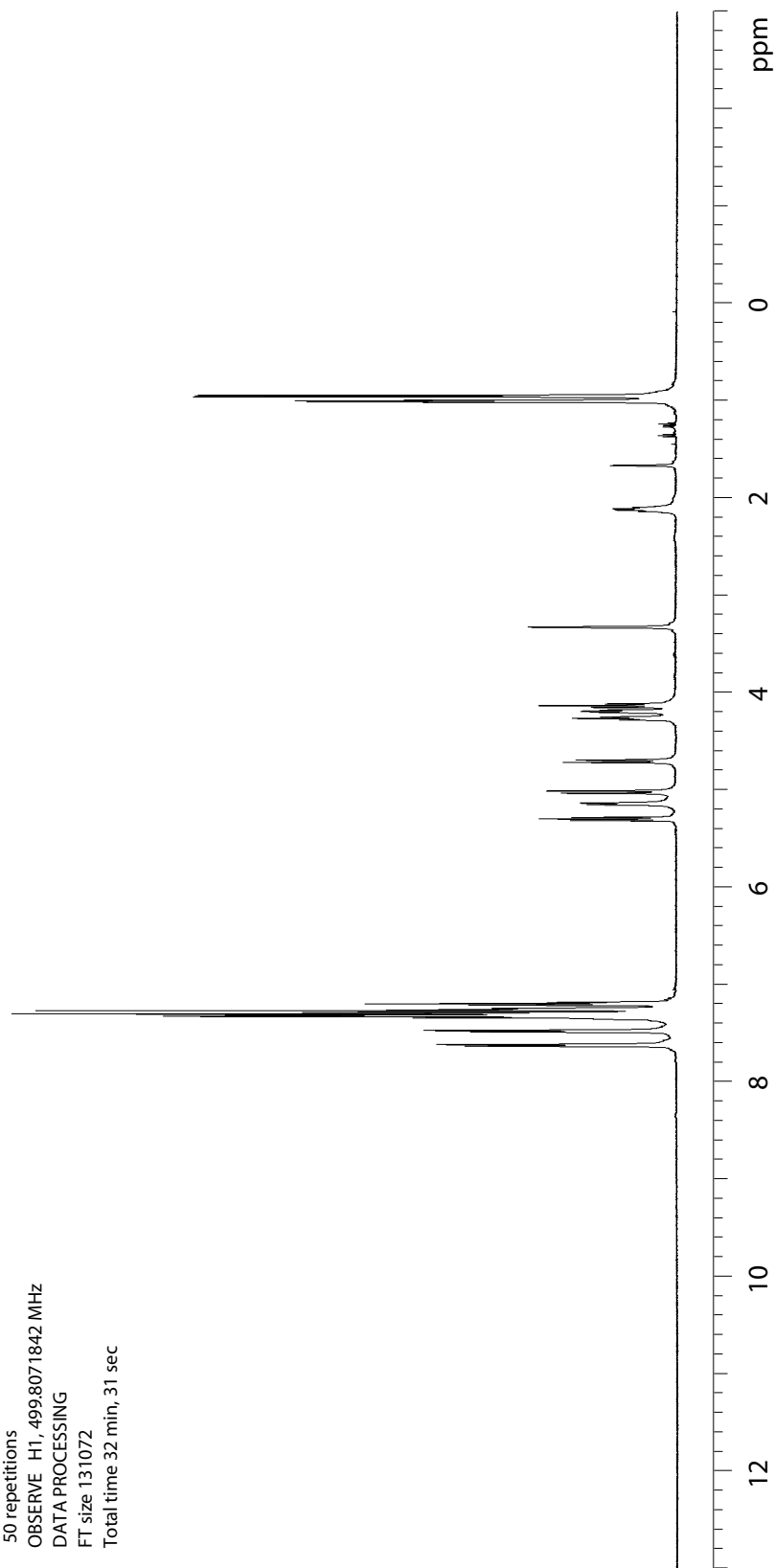
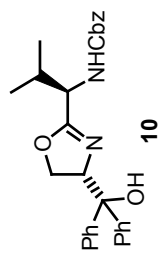
50 repetitions

OBSERVE H1, 499.8071842 MHz

DATA PROCESSING

FT size 131072

Total time 32 min, 31 sec



STANDARD CARBON PARAMETERS

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

User: 1-14-87

File: n9p205c

UNITY-500 "vxt500nm1"

Relax. delay 5.000 sec

Pulse 51.9 degrees

Acq. time 1.300 sec

Width 25000.0 Hz

1345 repetitions

OBSERVE C13, 125.6765879 MHz

DECOUPLE H1, 499.8096844 MHz

Power 33 dB

continuously on

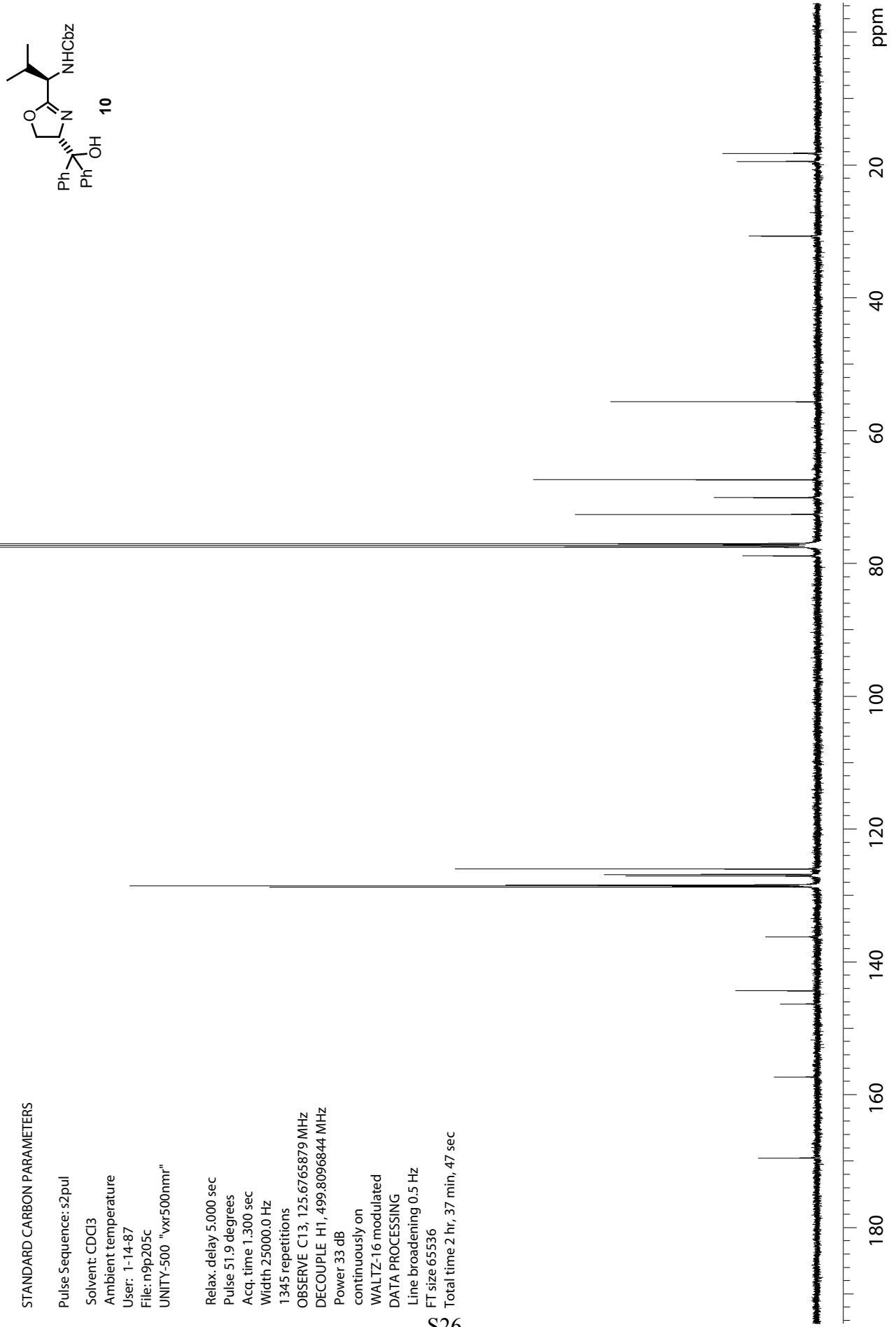
WALTZ-16 modulated

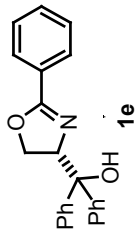
DATA PROCESSING

Line broadening 0.5 Hz

FT size 65536

Total time 2 hr, 37 min, 47 sec





STANDARD PROTON PARAMETERS

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

File: n10p129

VXR-300S "vx1300b"

Relax. delay 5.000 sec

Pulse 45.0 degrees

Acq. time 8.000 sec

Width 8000.0 Hz

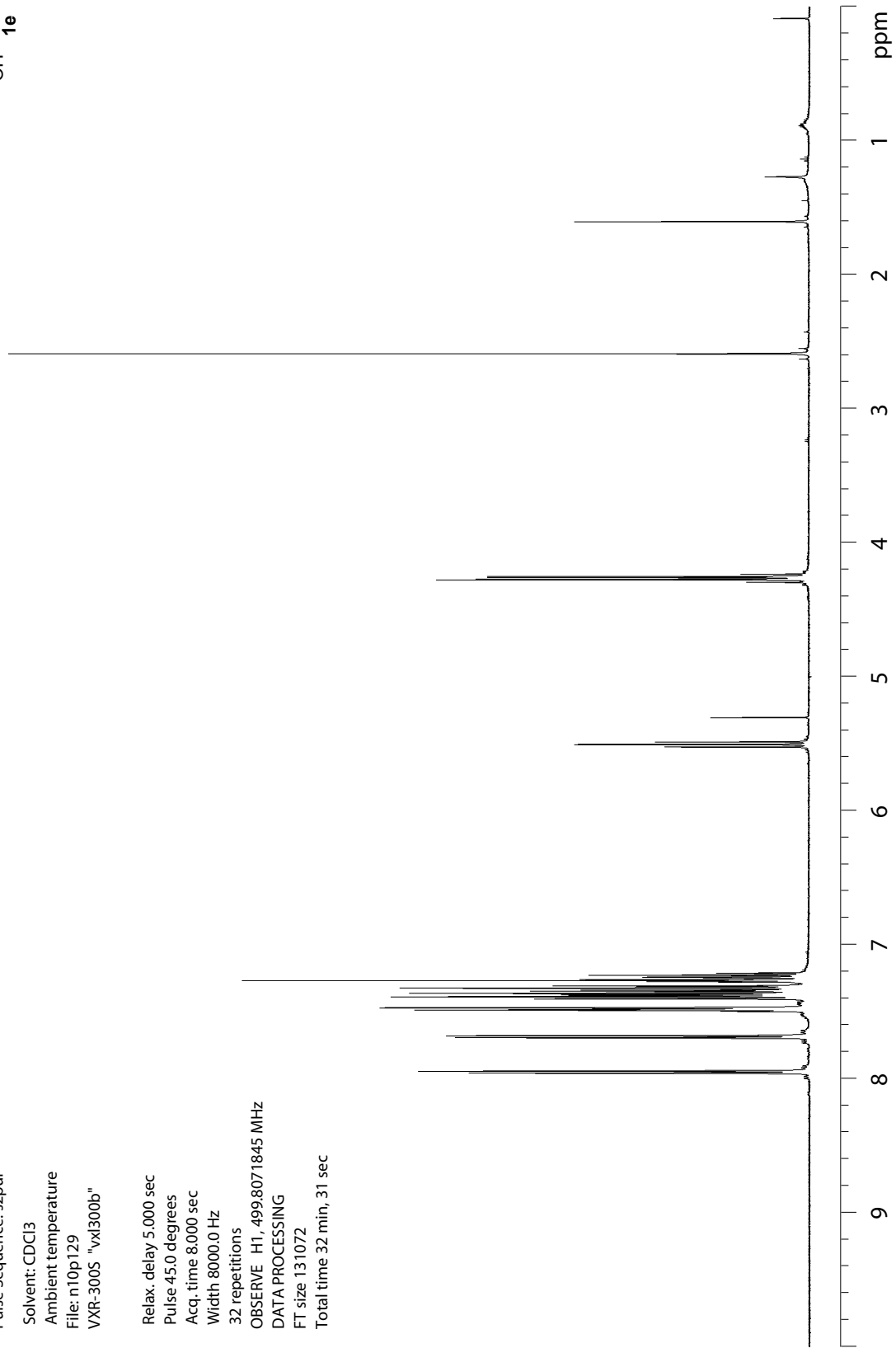
32 repetitions

OBSERVE H1, 499.8071845 MHz

DATA PROCESSING

FT size 131072

Total time 32 min, 31 sec



STANDARD CARBON PARAMETERS

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

User: 1-14-87

File: n10p129c

UNITY-500 "vxr500nmr"

Pulse 51.9 degrees

Acq. time 1.300 sec

Width 25000.0 Hz

940 repetitions

OBSERVE C13, 125.6765879 MHz

DECOUPLE H1, 499.8096844 MHz

Power 33 dB

continuously on

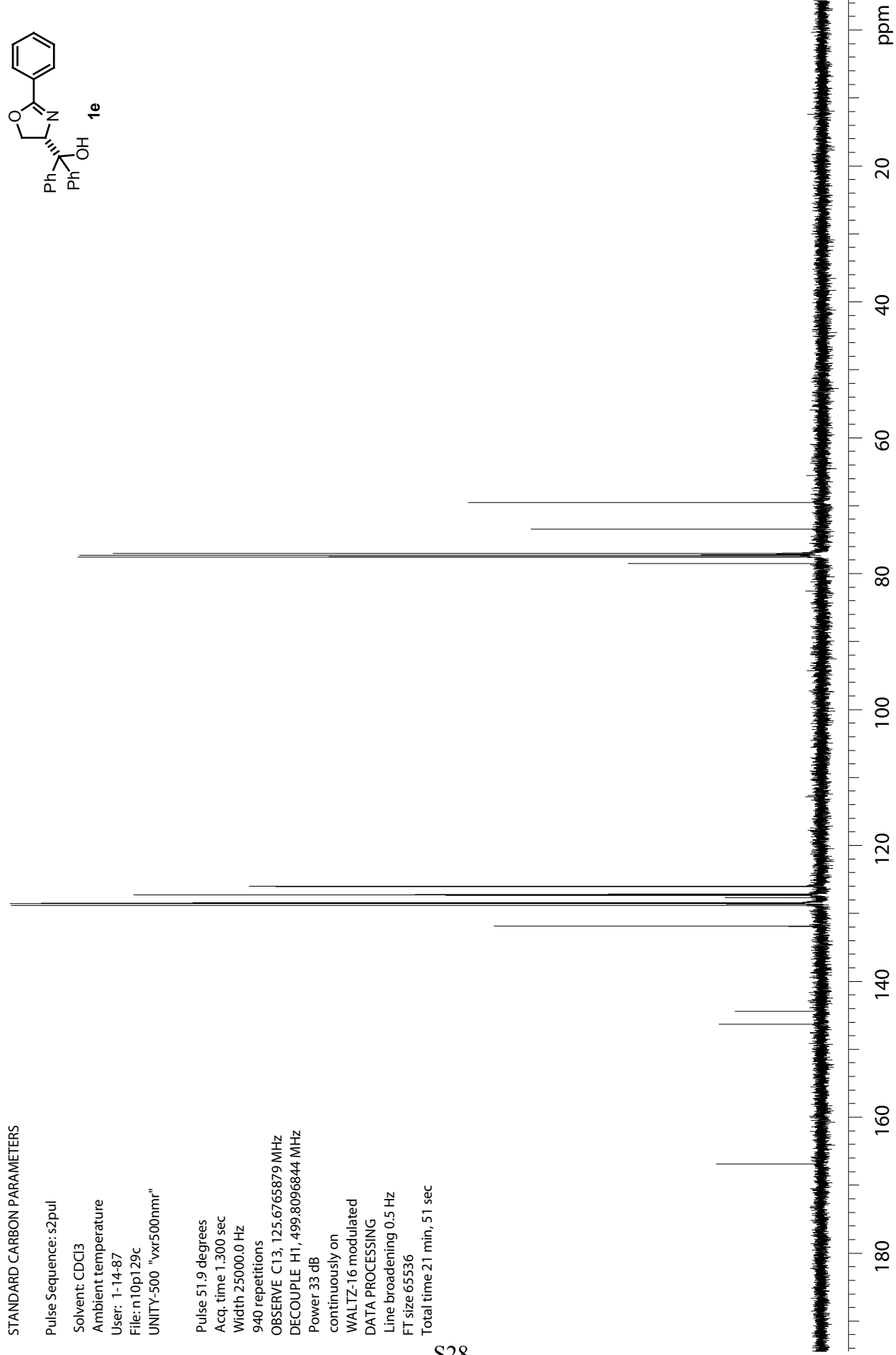
WALTZ-16 modulated

DATA PROCESSING

Line broadening 0.5 Hz

FT size 65536

Total time 21 min, 51 sec



STANDARD PROTON PARAMETERS

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

File: n9p47

VXR-3005 "vx1300b"

Relax. delay 5.000 sec

Pulse 45.0 degrees

Acq. time 8.000 sec

Width 8000.0 Hz

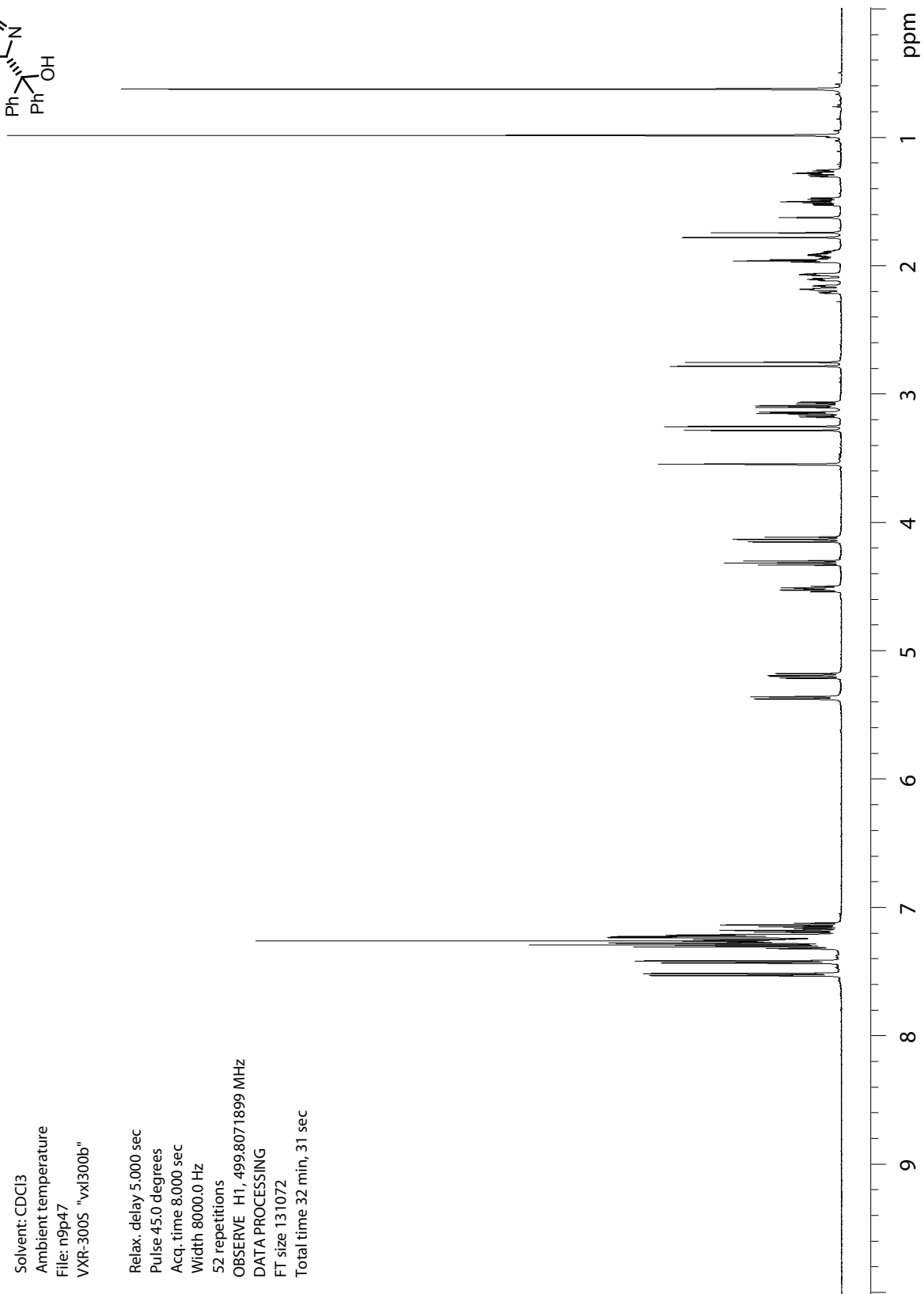
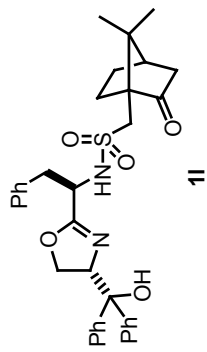
52 repetitions

OBSERVE H1, 499.8071899 MHz

DATA PROCESSING

FT size 131072

Total time 32 min, 31 sec



STANDARD CARBON PARAMETERS

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

User: 1-14-87

File: n9p47c

UNITY-500 "vyr500nm1"

Relax. delay 5.000 sec

Pulse 51.9 degrees

Acq. time 1.300 sec

Width 40000.0 Hz

410 repetitions

OBSERVE C13, 125.6765879 MHz

DECOUPLE H1, 499.8096844 MHz

Power 33 dB

continuously on

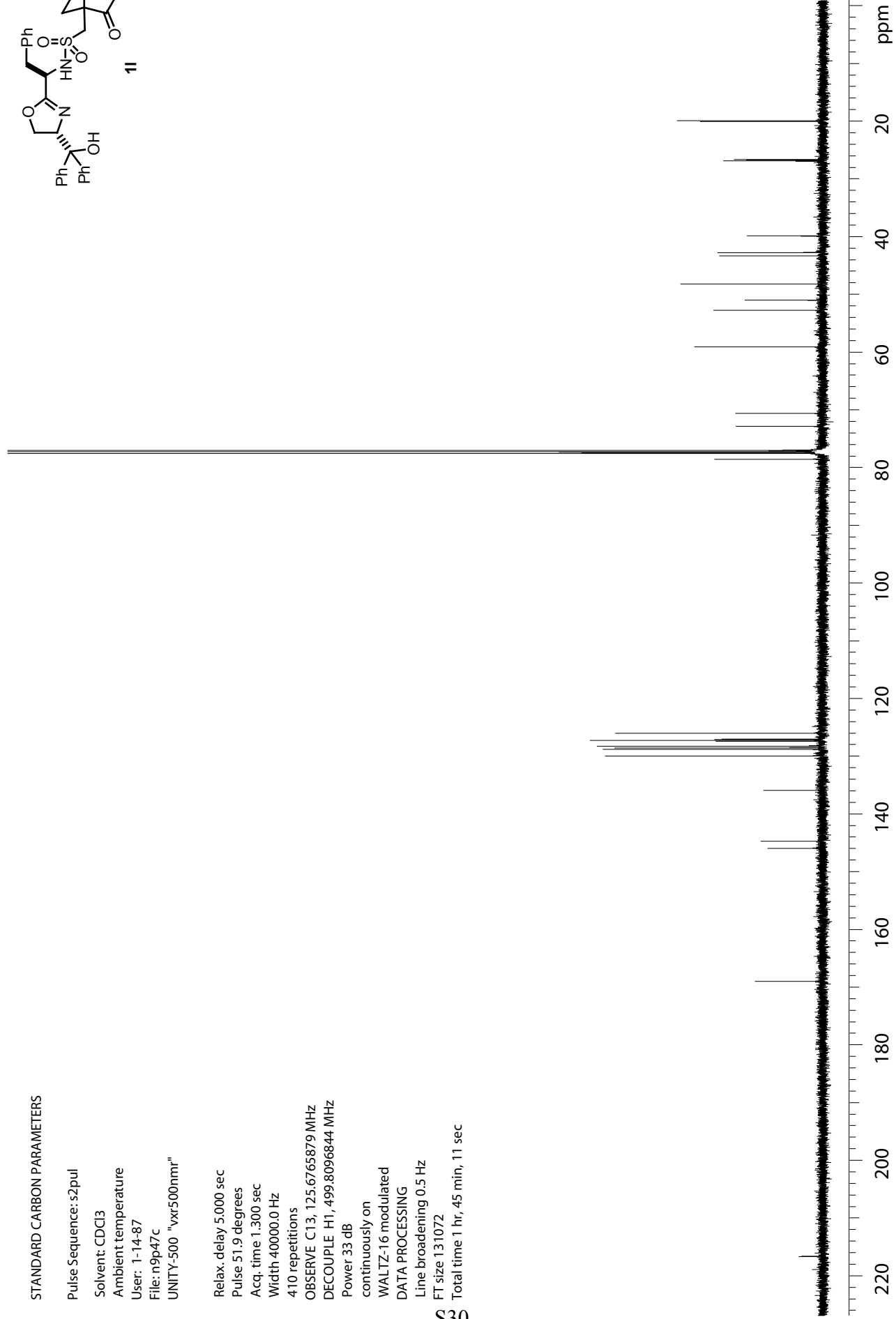
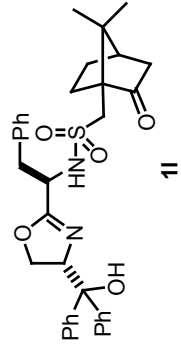
WALTZ-16 modulated

DATA PROCESSING

Line broadening 0.5 Hz

FT size 131072

Total time 1 hr, 45 min, 11 sec



N9P23

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

File: n9p23

VXR-300S "vx1300b"

Relax. delay 5.000 sec

Pulse 45.0 degrees

Acq. time 8.000 sec

Width 8000.0 Hz

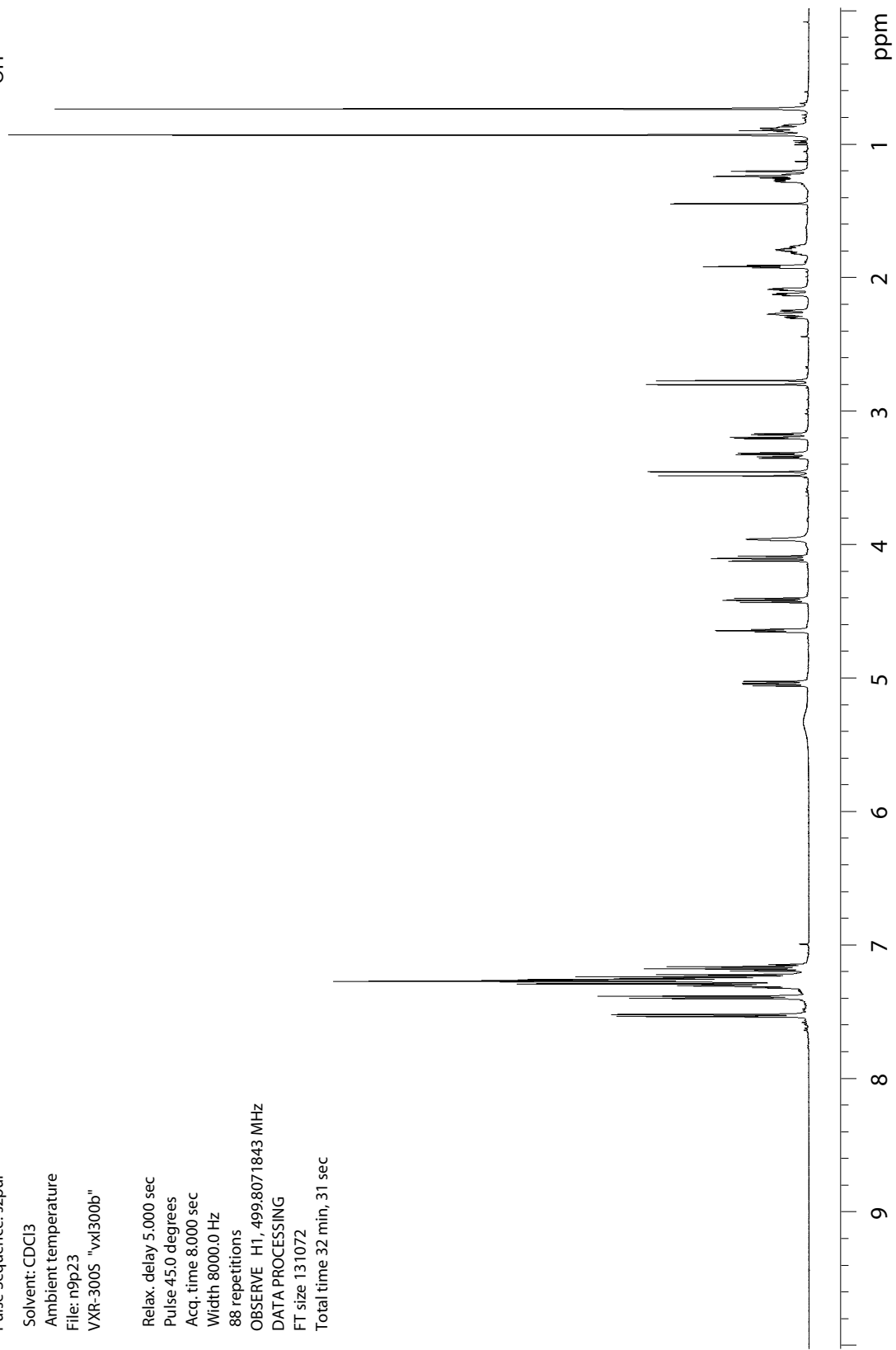
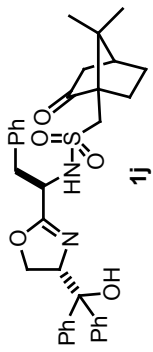
88 repetitions

OBSERVE H1, 499.8071843 MHz

DATA PROCESSING

FT size 131072

Total time 32 min, 31 sec



n9p23

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: 1-14-87
UNITY-500 "vyr500mmr"

Relax. delay 5.000 sec
Pulse 51.9 degrees
Acq. time 1.300 sec
Width 40000.0 Hz
490 repetitions

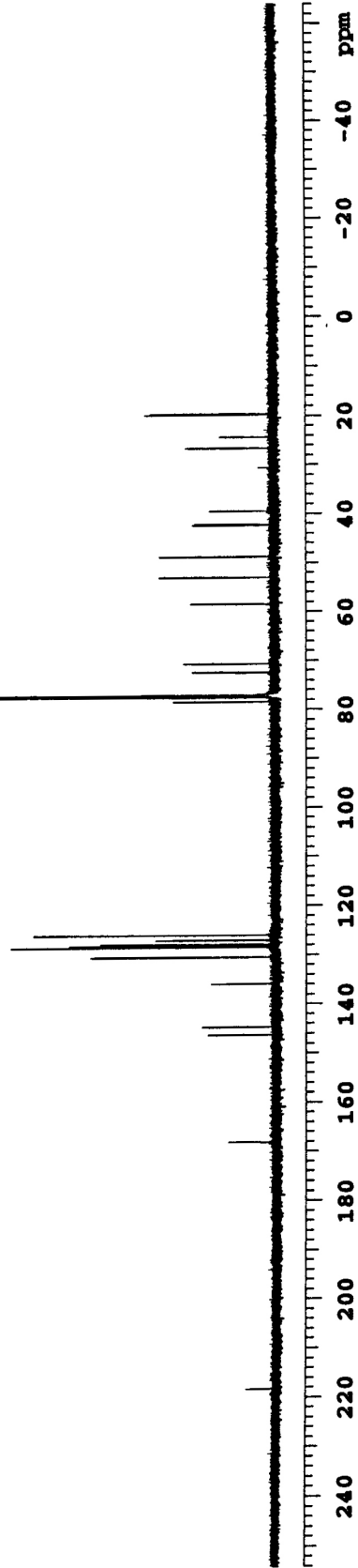
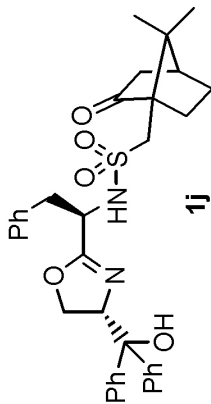
OBSERVE C13, 125.6765879 MHz
DECOUPLE H1, 499.8096844 MHz

Power 33 dB
continuously on
WALTZ-16 modulated

DATA PROCESSING

Line broadening 0.5 Hz
FT size 131072

Total time 2 hr, 37 min, 47 sec



phthallic acid -oxam-reaction

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

File: n10p49

VXR-3005 "vx1300b"

Relax. delay 5.000 sec

Pulse 45.0 degrees

Acq. time 8.000 sec

Width 8000.0 Hz

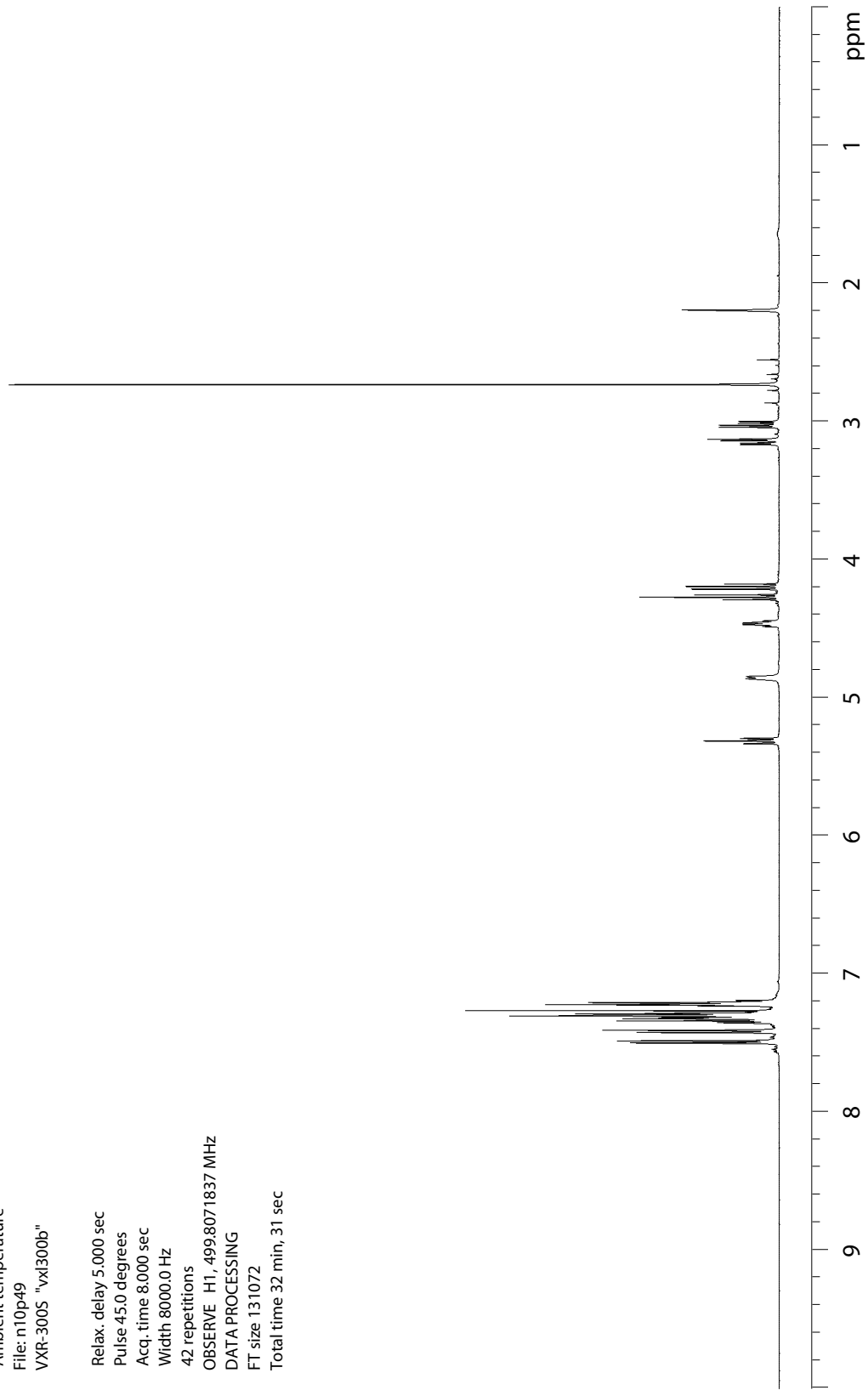
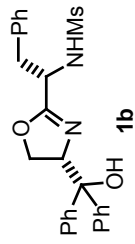
42 repetitions

OBSERVE H1, 499.8071837 MHz

DATA PROCESSING

FT size 131072

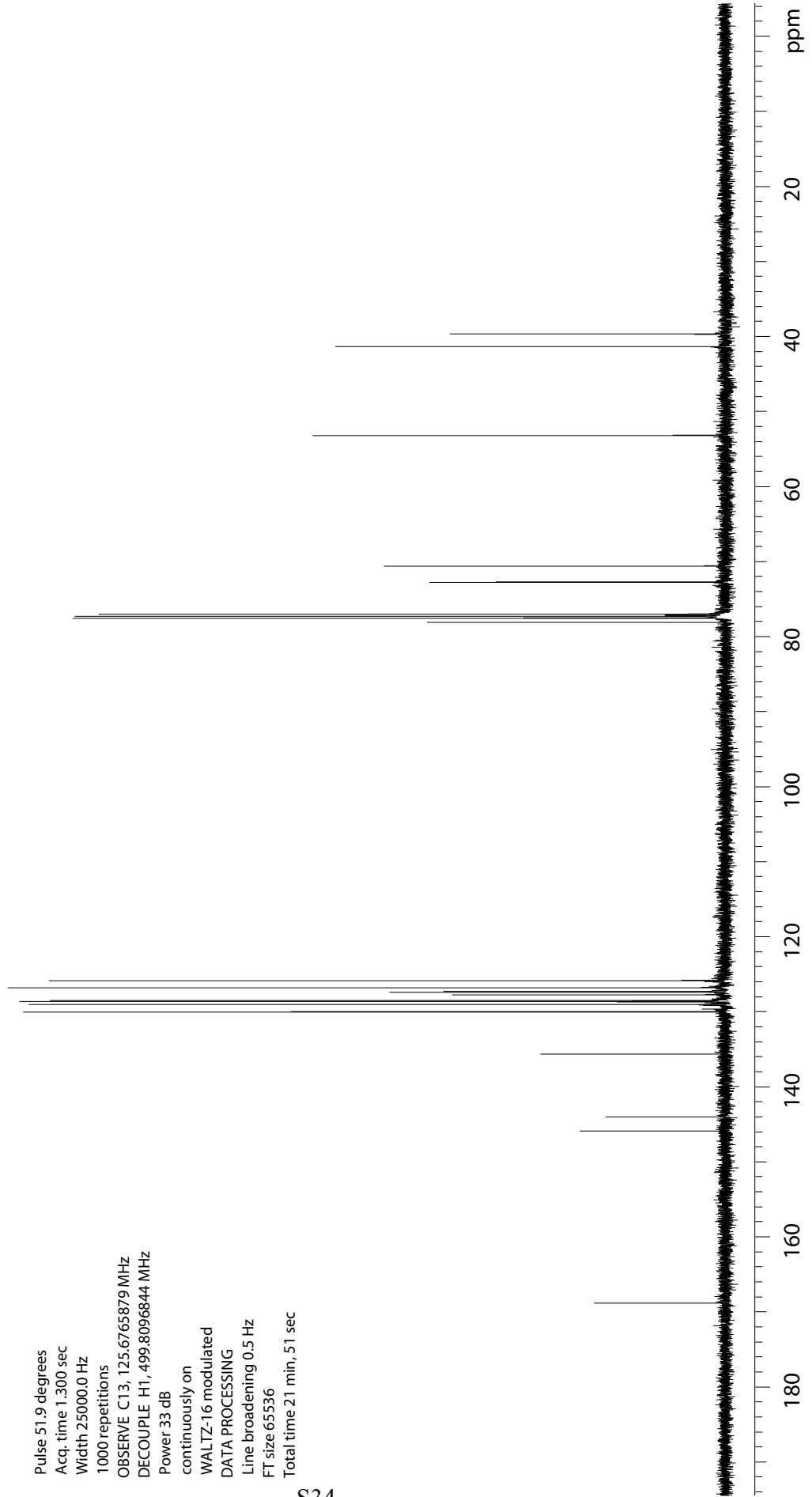
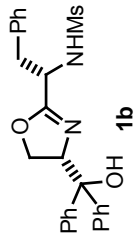
Total time 32 min, 31 sec



STANDARD CARBON PARAMETERS

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: 1-14-87
File: n10p49c
UNITY-300 "unity300nmr"

Pulse 51.9 degrees
Acq. time 1.300 sec
Width 25000.0 Hz
1000 repetitions
OBSERVE C13, 125.6765879 MHz
DECOUPLE H1, 499.8096844 MHz
Power 33 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 21 min, 51 sec



STANDARD CARBON PARAMETERS

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

User: 1-14-87

File: n9p125c

UNITY-300 "unity300nmr"

Relax. delay 5.000 sec

Pulse 51.9 degrees

Acq. time 1.300 sec

Width 40000.0 Hz

330 repetitions

OBSERVE C13, 125.6765879 MHz

DECOUPLE H1, 499.8096844 MHz

Power 33 dB

continuously on

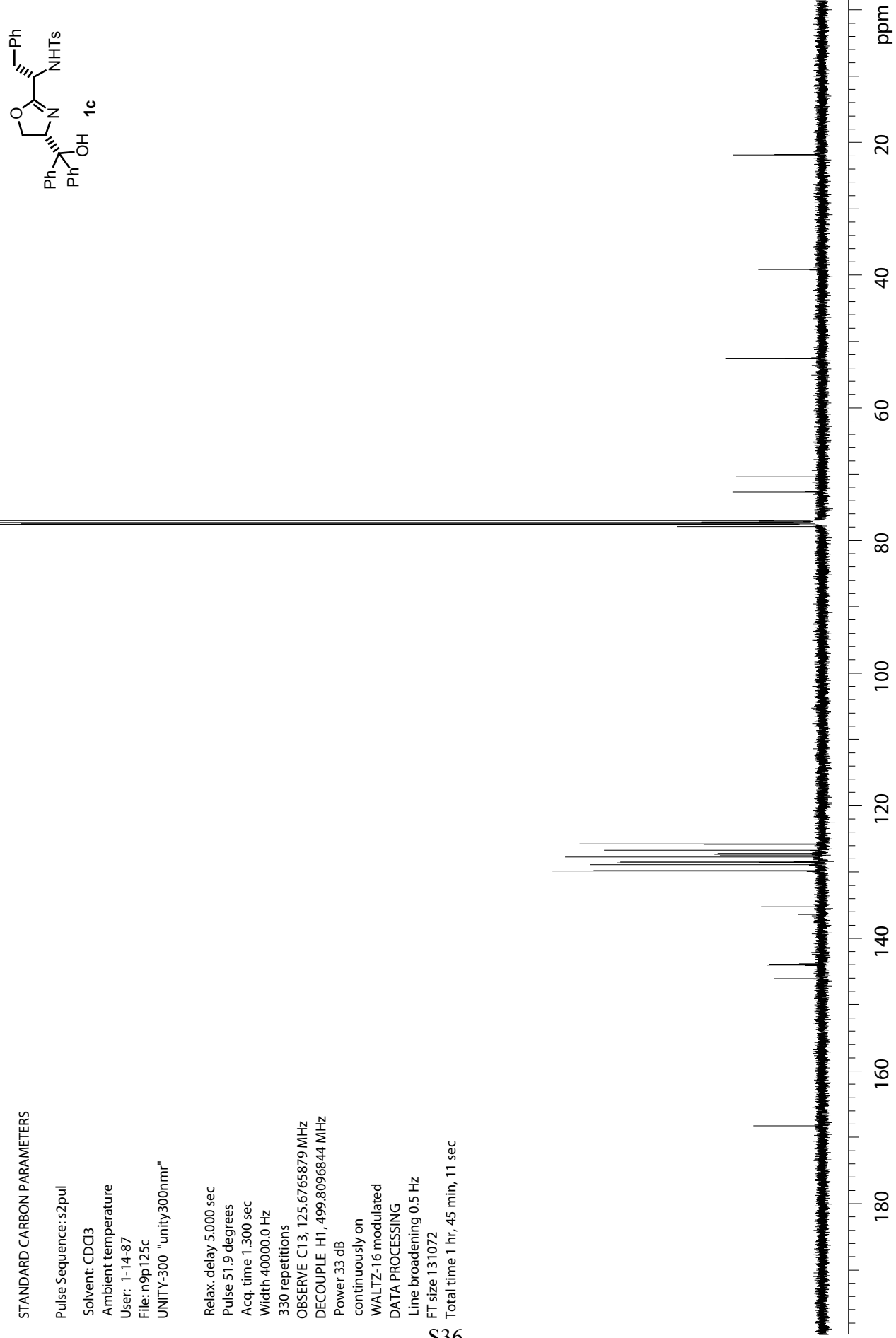
WALTZ-16 modulated

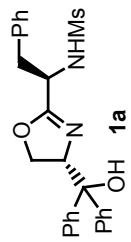
DATA PROCESSING

Line broadening 0.5 Hz

FT size 131072

Total time 1 hr, 45 min, 11 sec





STANDARD PROTON PARAMETERS

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

File: n10p59

VXR-300S "vx1300b"

Relax. delay 5.000 sec

Pulse 45.0 degrees

Acq. time 8.000 sec

Width 8000.0 Hz

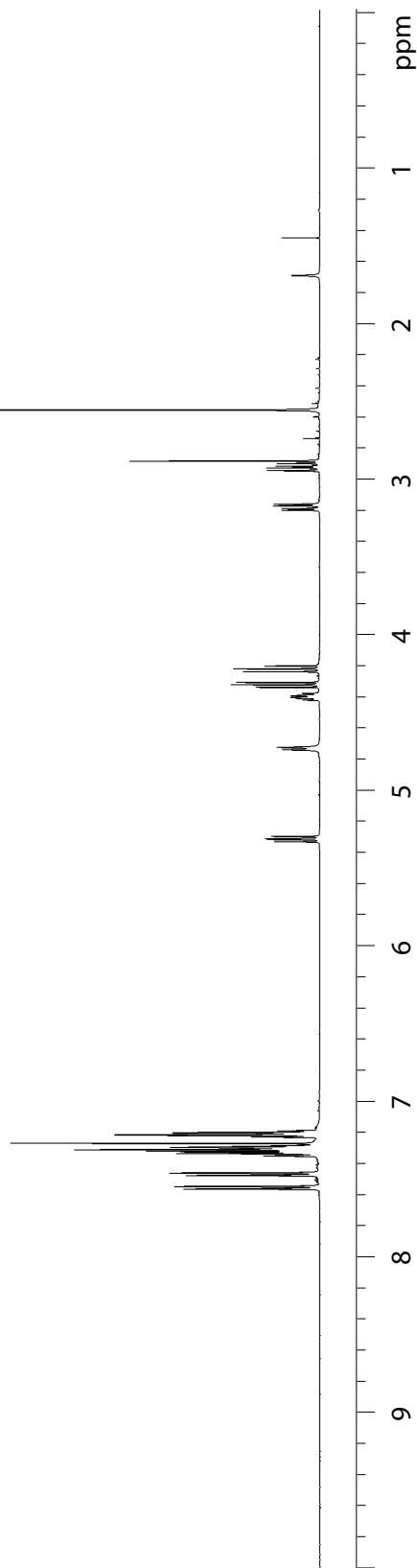
30 repetitions

OBSERVE H1, 499.8071844 MHz

DATA PROCESSING

FT size 131072

Total time 32 min, 31 sec



STANDARD CARBON PARAMETERS

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

User: 1-14-87

File: n10p59c

UNITY-300 "unity300nmr"

Pulse 51.9 degrees

Acq. time 1.300 sec

Width 25000.0 Hz

1000 repetitions

OBSERVE C13, 125.6765879 MHz

DECOUPLE H1, 499.8096844 MHz

Power 33 dB

continuously on

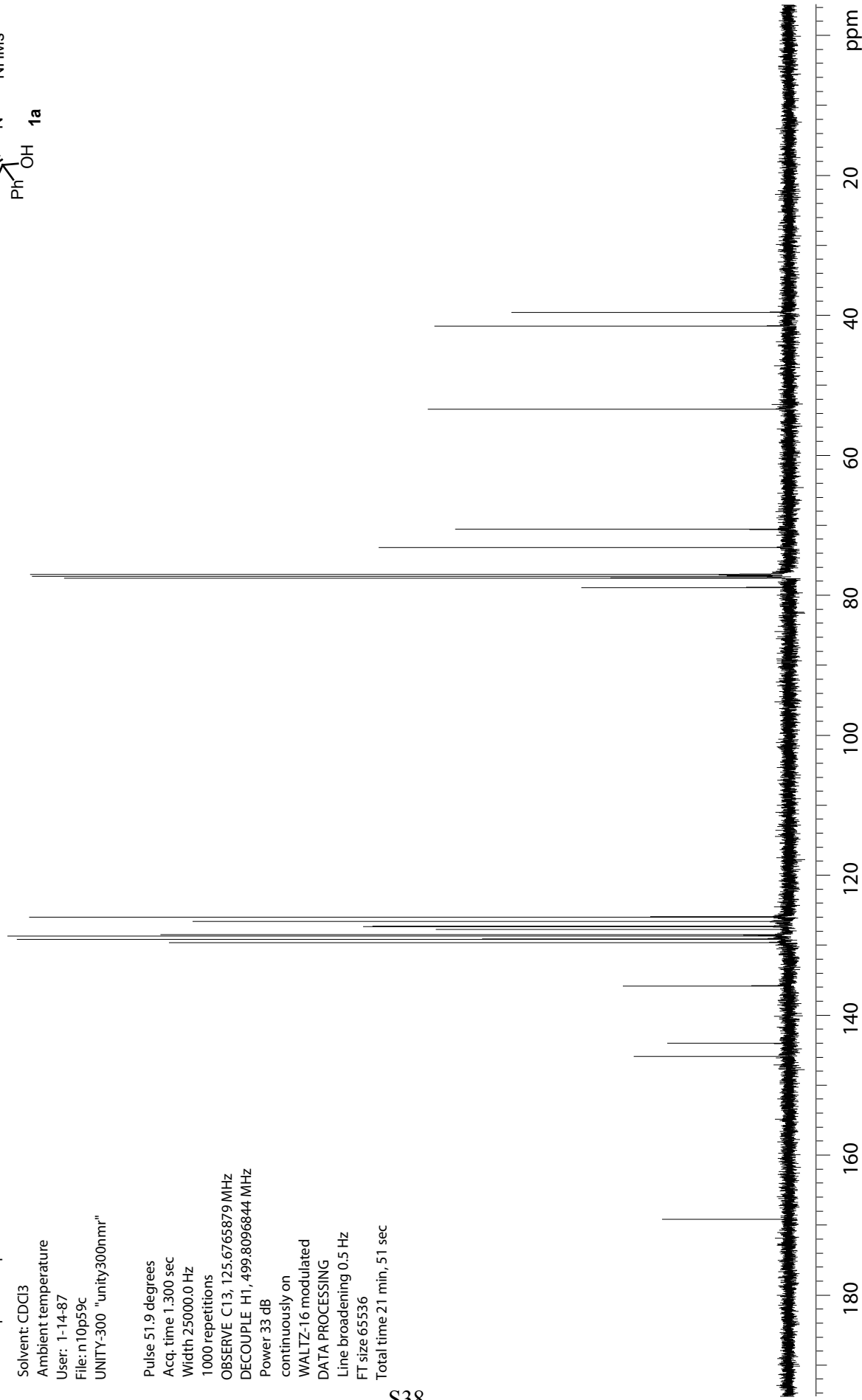
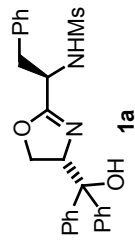
WALTZ-16 modulated

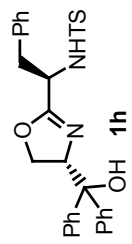
DATA PROCESSING

Line broadening 0.5 Hz

FT size 65536

Total time 21 min, 51 sec





n10p61

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

File: n10p61

VXR-300S "vx1300b"

Relax. delay 5.000 sec

Pulse 45.0 degrees

Acq. time 8.000 sec

Width 8000.0 Hz

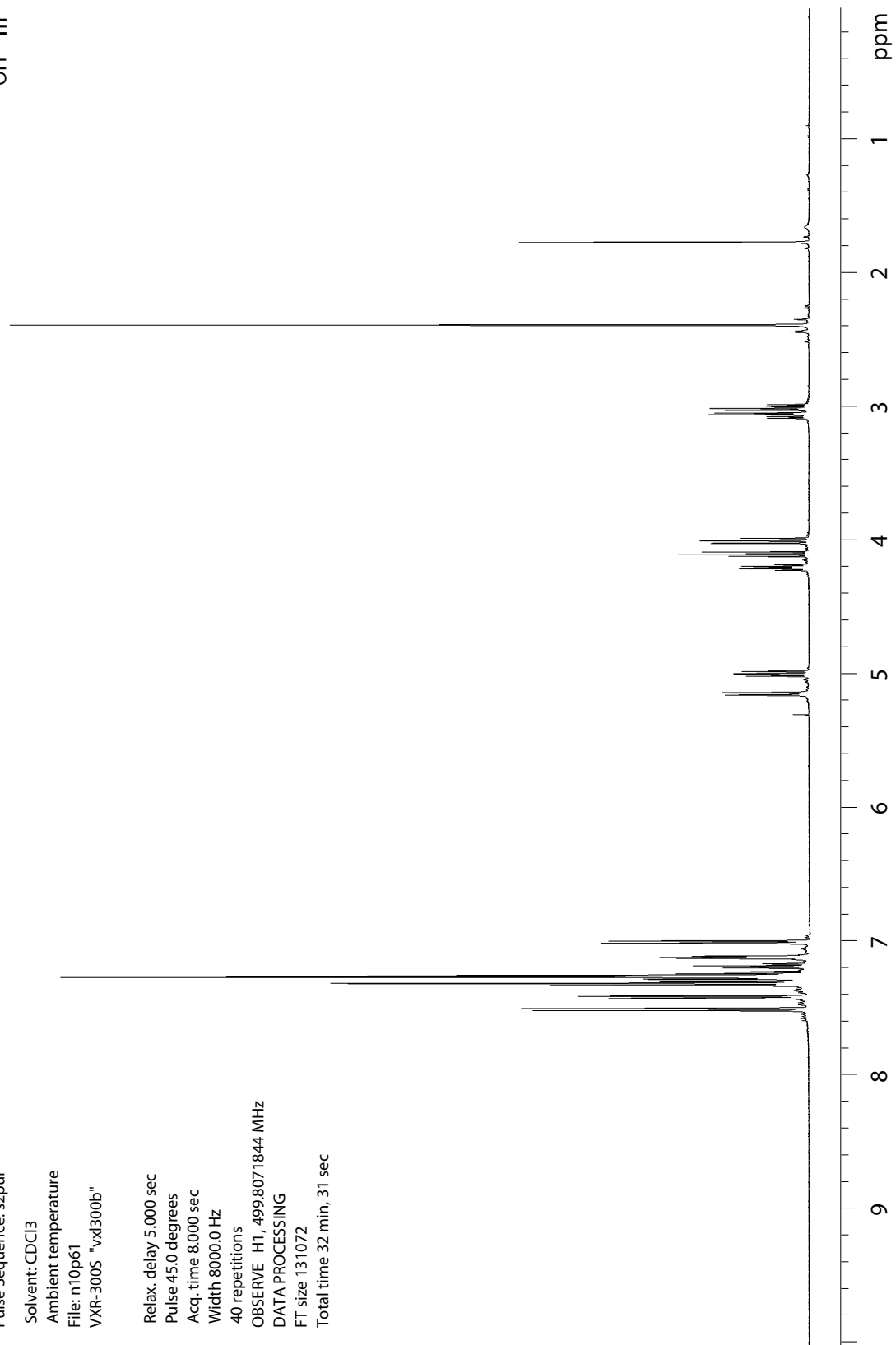
40 repetitions

OBSERVE H1, 499.8071844 MHz

DATA PROCESSING

FT size 131072

Total time 32 min, 31 sec



n10p61c

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

User: 1-14-87

File: n10p61c

UNITY-300 "unity300nmr"

Pulse 51.9 degrees

Acq. time 1.300 sec

Width 25000.0 Hz

980 repetitions

OBSERVE C13, 125.6765879 MHz

DECOUPLE H1, 499.8096844 MHz

Power 33 dB

continuously on

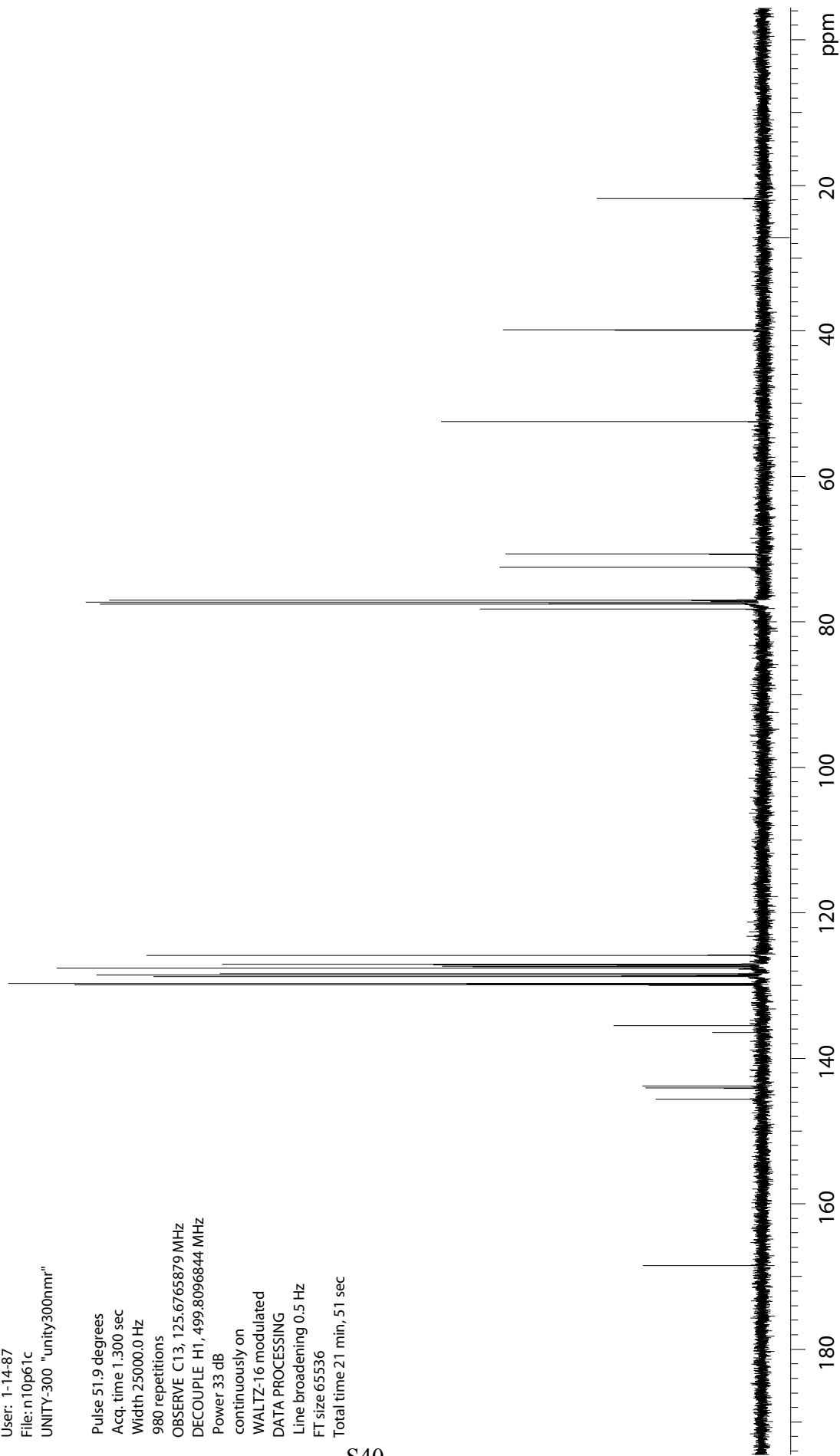
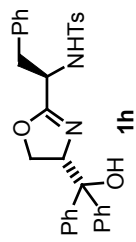
WALTZ-16 modulated

DATA PROCESSING

Line broadening 0.5 Hz

FT size 65536

Total time 21 min, 51 sec



STANDARD PROTON PARAMETERS

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

File: n10p63

VXR-300S "vx1300b"

Relax. delay 5.000 sec

Pulse 45.0 degrees

Acq. time 8.000 sec

Width 8000.0 Hz

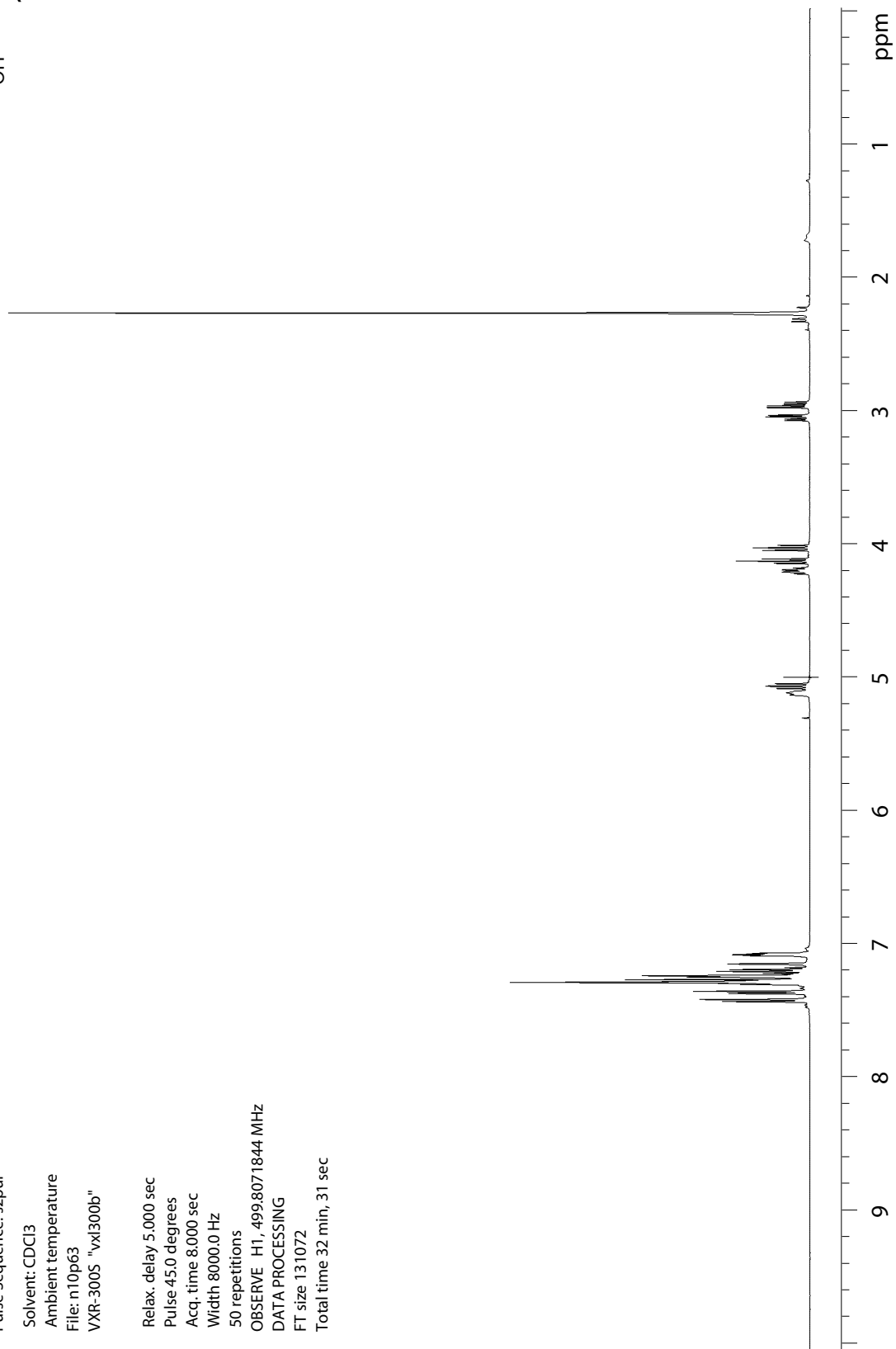
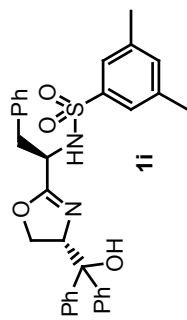
50 repetitions

OBSERVE H1, 499.8071844 MHz

DATA PROCESSING

FT size 131072

Total time 32 min, 31 sec



STANDARD PROTON PARAMETERS

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

File: n8p303

VXR-300S "vx1300b"

Relax. delay 4.000 sec

Pulse 45.0 degrees

Acq. time 8.000 sec

Width 8000.0 Hz

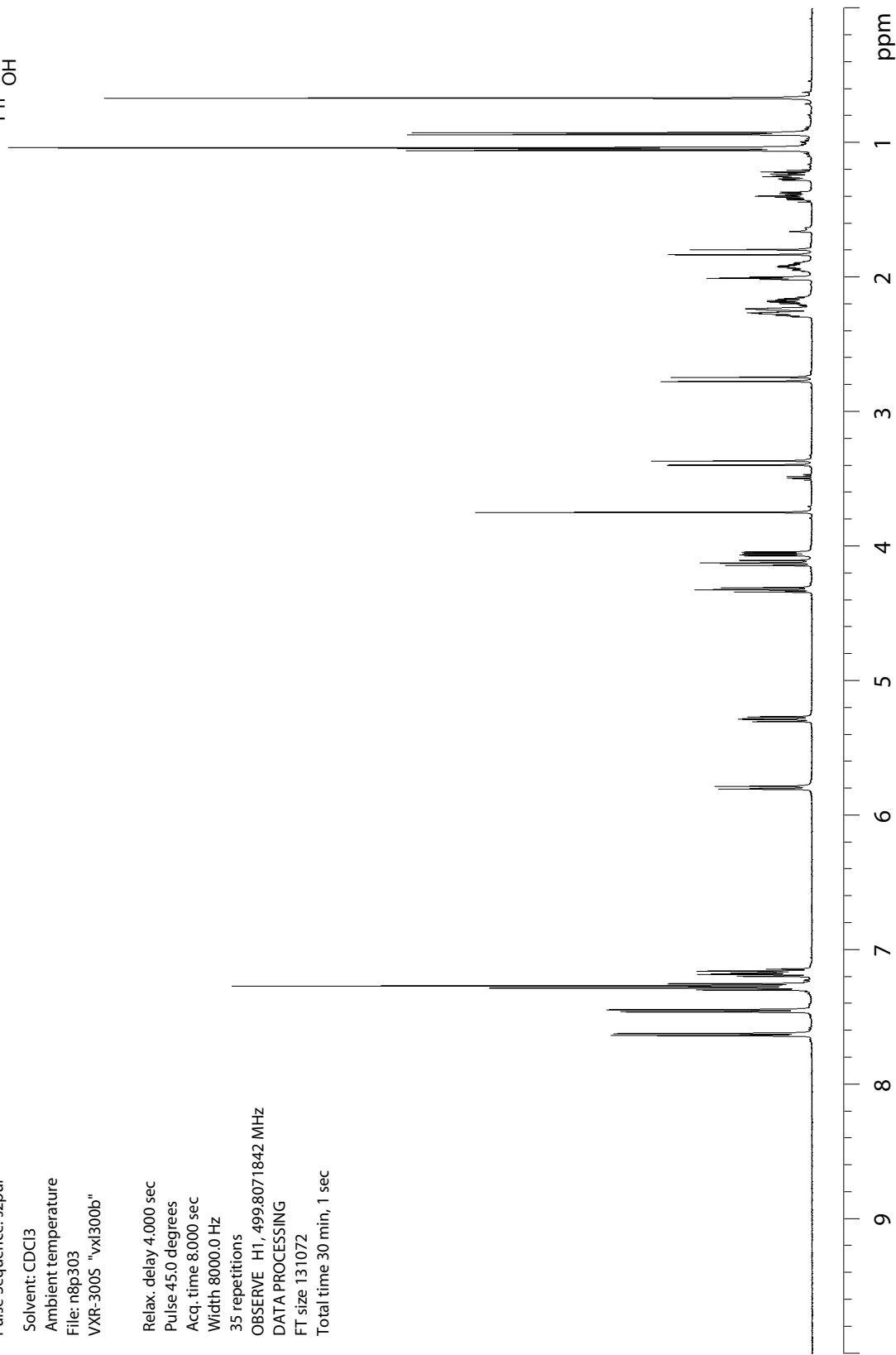
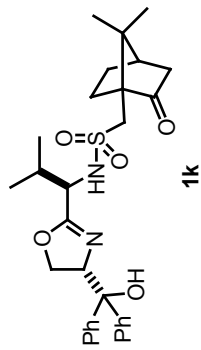
35 repetitions

OBSERVE H1, 499.8071842 MHz

DATA PROCESSING

FT size 131072

Total time 30 min, 1 sec



STANDARD CARBON PARAMETERS

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

User: 1-14-87

File: n8p303c

UNITY-500 "vvr500nm1"

Relax. delay 5.000 sec

Pulse 51.9 degrees

Acq. time 1.300 sec

Width 40000.0 Hz

140 repetitions

OBSERVE C13, 125.6765879 MHz

DECOUPLE H1, 499.8096844 MHz

Power 33 dB

continuously on

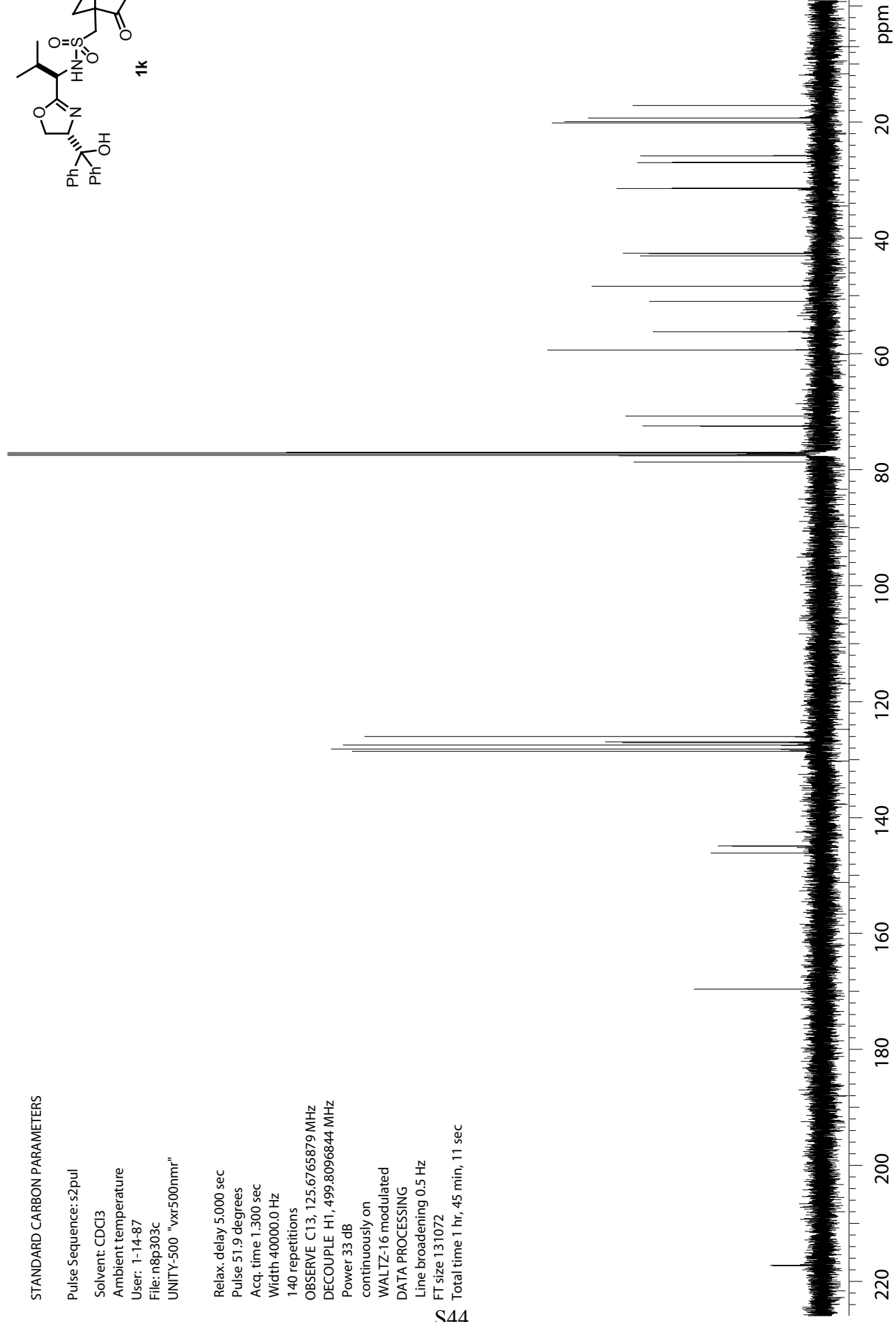
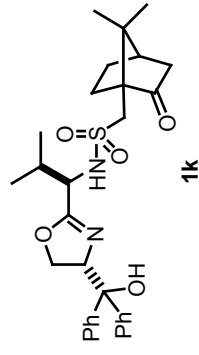
WALTZ-16 modulated

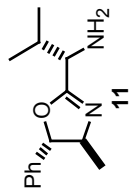
DATA PROCESSING

Line broadening 0.5 Hz

FT size 131072

Total time 1 hr, 45 min, 11 sec





STANDARD PROTON PARAMETERS

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

File: n9p123

VXR-300S "vx1300b"

Relax. delay 6.000 sec

Pulse 45.0 degrees

Acq. time 8.000 sec

Width 8000.0 Hz

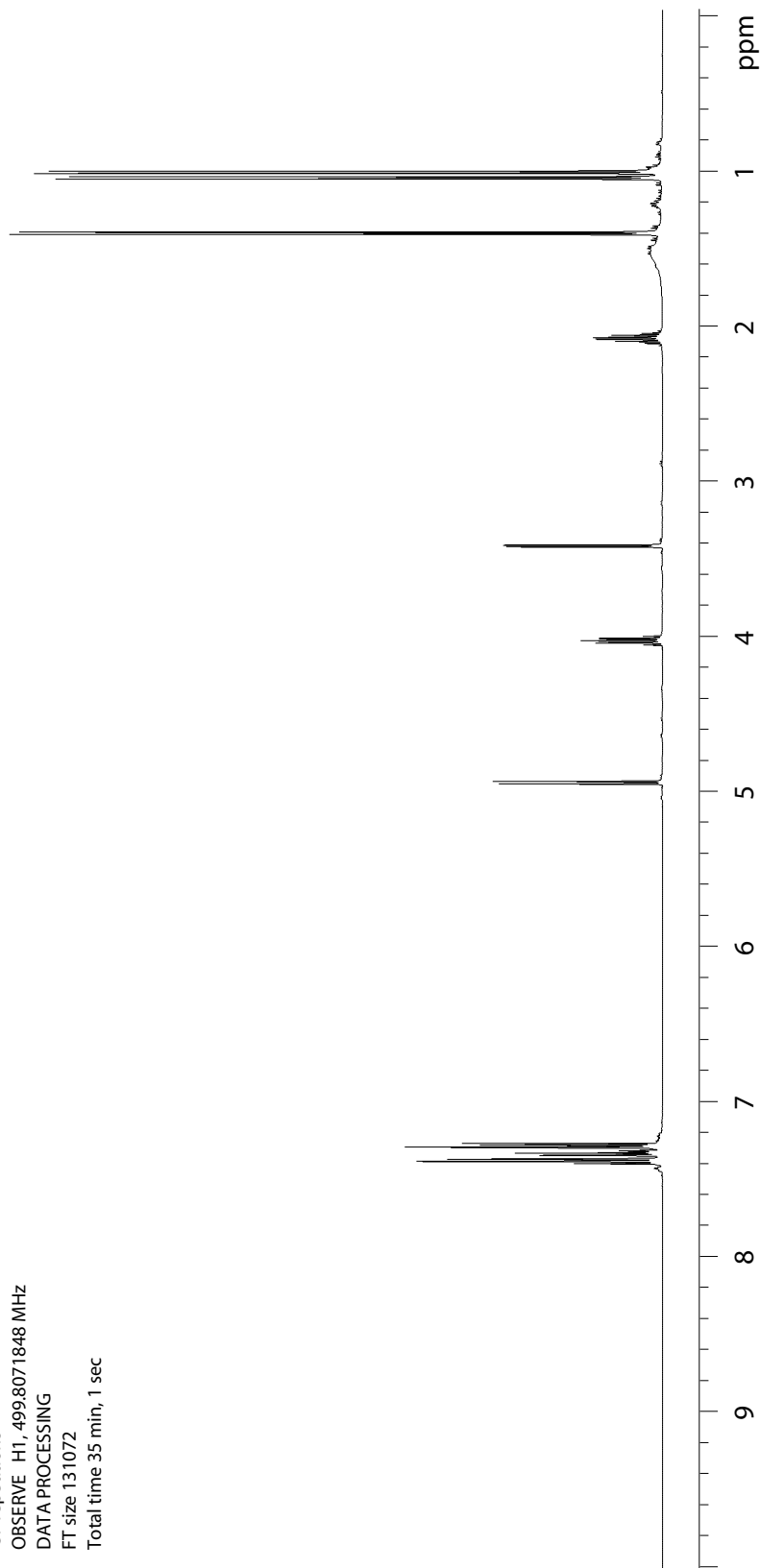
37 repetitions

OBSERVE H1, 499.8071848 MHz

DATA PROCESSING

FT size 131072

Total time 35 min, 1 sec



STANDARD PROTON PARAMETERS

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

File: n8p181

VXR-3005 "vxl300b"

Relax. delay 2.000 sec

Pulse 73.0 degrees

Acq. time 1.892 sec

Width 8000.0 Hz

56 repetitions

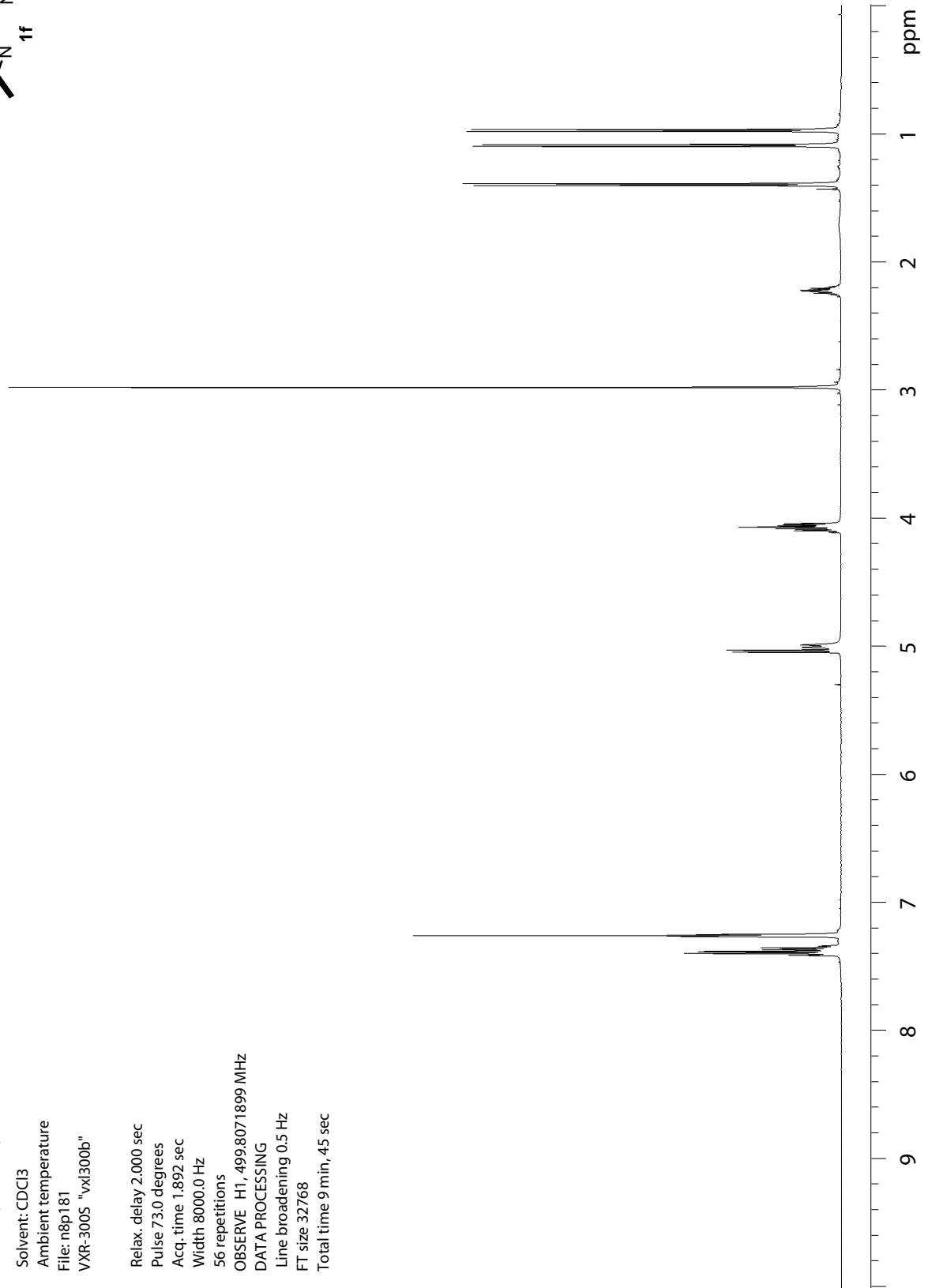
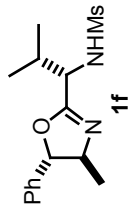
OBSERVE H1, 499.8071899 MHz

DATA PROCESSING

Line broadening 0.5 Hz

FT size 32768

Total time 9 min, 45 sec



STANDARD CARBON PARAMETERS

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

User: 1-14-87

File: n8p181C

UNITY-500 "vxr500nmr"

Relax. delay 3.000 sec

Pulse 51.9 degrees

Acq. time 1.300 sec

Width 25000.0 Hz

270 repetitions

OBSERVE C13, 125.6765879 MHz

DECOUPLE H1, 499.8096844 MHz

Power 33 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 0.5 Hz

FT size 65536

Total time 1 hr, 11 min, 51 sec

