Total Synthesis of (–)-*N*-Methylwelwitindolinone B Isothiocyanate via a Chlorinative Oxabicycle Ring-Opening Strategy

Nicholas A. Weires, Evan D. Styduhar,

Emma L. Baker, and Neil K. Garg*

Department of Chemistry and Biochemistry,

University of California, Los Angeles, CA 90095

Supporting Information – Table of Contents

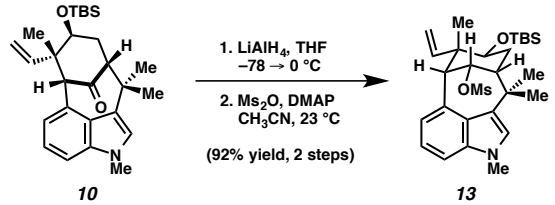
Materials and Methods. Unless stated otherwise, reactions were conducted in flame-dried glassware under an atmosphere of nitrogen using anhydrous solvents (either freshly distilled or passed through activated alumina columns). All commercially available reagents were used as received unless otherwise specified. $LiAlD_4$ was obtained from Acros. AgOTf and Schwartz' reagent were obtained from Strem. Bathophenanthroline and selenium metal were obtained from Alfa Aesar. Ms_2O and BCl_3 were obtained from Aldrich. Petasis reagent[1] and Dess–Martin periodinane[2] were prepared from known literature procedures. Unless stated otherwise, reactions were performed at room temperature (rt, approximately 23 °C). Thin-layer chromatography (TLC) was conducted with EMD gel 60 F254 pre-coated plates (0.25 mm) and visualized using a combination of UV, anisaldehyde, iodine, and potassium permanganate staining. Silicycle silica gel 60 (particle size 0.040–0.063 mm) was used for flash column chromatography. ^{1}H and 2D NMR spectra were recorded on Bruker spectrometers (500 MHz). Data for ^{1}H spectra are reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz), integration and are referenced to the residual solvent peak 7.26 ppm for $CDCl_3$ and 7.16 for C_6D_6. Data for ^{2}H NMR spectra are reported as follows: chemical shift (δ ppm, at 77 MHz), multiplicity, coupling constant, integration and are referenced to the residual solvent peak 7.26 ppm for $CDCl_3$. ^{13}C NMR spectra are reported in terms of chemical shift (at 125 MHz) and are referenced to the residual solvent peak 77.16 ppm for $CDCl_3$.[3] IR spectra were recorded on a Perkin-Elmer 100 spectrometer and a JASCO 4100 spectrometer and are reported in terms of frequency absorption (cm^{-1}). Optical rotations were measured with a Rudolph Autopol III Automatic Polarimeter. Uncorrected melting points were measured using a Mel-Temp II melting point apparatus with a Fluke 50S thermocouple and a Digimelt MPA160 melting point apparatus. High resolution mass spectra were obtained from the UC Irvine Mass Spectrometry Facility and the UCLA Molecular Instrumentation Center.

Complete Reference 4r from manuscript:

Freeman, D. B.; Holubec, A. A.; Weiss, M. W.; Dixon, J. A.; Kafefuda, A.; Ohtsuka, M.; Inoue, M.; Vaswani R. G.; Ohki, H.; Doan, B. D.; Reisman, S. E.; Stoltz, B. M.; Day, J. J.; Tao, R. N.; Dieterich, N. A.; Wood, J. L. *Tetrahedron* **2010**, *66*, 6647–6655.

[1] Payack, J. F.; Hughed, D. L.; Cai, D.; Cottrell, I. F.; Verhoeven, T. R. *Org. Synth.* **2002**, *79*, 19–22.
[2] Niu, C.; Pettersson, T.; Miller, M. J. *J. Org. Chem.* **1996**, *61*, 1014–1022.
[3] For compound **2** the ^{13}C NMR residual solvent peak is set to 77.0 ppm to match the reference values set in the isolation paper.

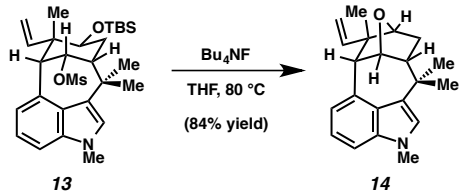
Experimental Procedures.



10 ***13***

Mesylate 13. To a solution of indole **10**[4] (500 mg, 1.14 mmol, 1.0 equiv) in THF (38.0 mL) at –78 °C was added a solution of $LiAlH_4$ (1.0 M in THF, 3.44 mL, 3.44 mmol, 3.0 equiv) in a dropwise manner. After stirring at –78 °C for 5 min, the solution was then allowed to warm to 0 ºC. After 20 min, the reaction was slowly quenched at 0 °C by the dropwise addition of a saturated solution of aqueous Rochelle's salt (30 mL), and then allowed to warm to 23 ºC. The resulting biphasic mixture was stirred at room temperature for 30 min, transferred to a separatory funnel with EtOAc (30 mL) and H_2O (30 mL), and extracted with EtOAc (3 x 20 mL). The organic layers were combined, dried over Na_2SO_4, and evaporated under reduced pressure. The resulting residue was used in the subsequent step without further purification.

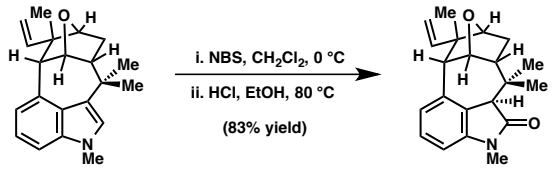
To a flask containing the crude product (382 mg, 0.87 mmol, 1.0 equiv) from the previous step was added DMAP (637 mg, 5.22 mmol, 6.0 equiv) and Ms_2O (409 mg, 2.35 mmol, 2.7 equiv) as solids. The flask was flushed with N_2, and CH_3CN (7.77 mL) was added. The reaction mixture was allowed to stir at room temperature. After 2 h the reaction was filtered by passage through a plug of silica gel (5:1 hexanes:EtOAc eluent) to afford mesylate **13** (413 mg, 92% yield, over two steps) as a white foam. Mesylate **13**: mp: 71.5 ºC; R_f 0.53 (5:1 hexanes:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.17 (dd, *J* = 8.1, 0.6, 1H), 7.06 (dd, *J* = 8.1, 7.2, 1H), 6.95 (s, 1H), 6.66 (d, *J* = 7.1, 1H), 5.79 (app t, *J* = 5.8, 1H), 4.92 (dd, *J* = 17.5, 1.1, 1H), 4.78 (dd, *J* = 11.0, 1.1, 1H), 4.44 (dd, *J* = 17.4, 10.9, 1H), 4.77 (s, 3H), 3.64 (dd, *J* = 12.3, 4.2, 1H), 3.33 (d, *J* = 5.4, 1H), 2.85 (s, 3H), 2.55–2.48 (m, 1H), 2.18 (ddd, *J* = 14.7, 4.0, 2.7, 1H), 1.95 (ddd, *J* = 14.7, 12.4, 5.6, 1H), 1.57 (s, 3H), 1.42 (s, 3H), 1.36 (s, 3H), 0.73 (s, 9H), –0.16 (s, 3H), –0.38 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 146.8, 136.7, 130.5, 126.4, 125.7, 124.4, 124.2, 120.5, 112.5, 107.8, 82.4, 68.2, 57.7, 49.2, 48.7, 40.5, 39.1, 37.4, 33.0, 32.8, 32.0, 25.9, 18.0, 16.1, -4.0, -4.6; IR (film): 2952, 2895, 1607, 1533, 1472 cm^{-1}; HRMS-ESI (*m/z*) $[M + H]^+$ calcd for $C_{28}H_{44}NO_4SSi$, 518.27603; found 518.27472; $[\alpha]^{21.6}_D$ +59.60° (*c* = 1.000, $CHCl_3$).



13 ***14***

[4] Huters, A. D.; Quasdorf, K. W.; Styduhar, E. D.; Garg, N. K. *J. Am. Chem. Soc.* **2011**, *133*, 15797–15799.

Oxabicycle 14. To a Schlenk tube containing a solution of mesylate **13** (118 mg, 0.23 mmol, 1.0 equiv) in THF (5.8 mL) was added TBAF (1.0 M in THF, 681 μL, 0.68 mmol, 3.0 equiv) in a dropwise manner. The Schlenk tube was then sealed and heated to 80 °C. After 21 h, the solution was allowed to cool to 23 ºC and then filtered by passage over a plug of silica gel (EtOAc eluent, 30 mL). The filtrate was concentrated and the resulting residue was purified by flash chromatography (9:1 hexanes:EtOAc) to afford oxabicycle **14** (56 mg, 84% yield) as a white solid. Oxabicycle **14**: mp: 108.8 ºC; R_f 0.66 (3:1 hexanes:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.16–7.08 (m, 2H), 6.91 (s, 1H), 6.72 (d, *J* = 6.4, 1H), 4.93 (app t, *J* = 4.4, 1H), 4.75–4.71 (m, 1H), 4.65–4.59 (m, 1H), 4.55–4.52 (m, 1H), 4.16 (d, *J* = 6.1, 1H), 3.75 (s, 3H), 3.46 (d, *J* = 5.3, 1H), 2.44–2.34 (m, 1H), 1.89–1.83 (ddd, *J* = 23.8, 11.8, 6.3, 1H), 1.64–1.60 (dd, *J* = 12.4, 8.5, 1H), 1.43 (s, 3H), 1.37 (s, 3H), 1.23 (s, 3H); ^{13}C NMR (500 MHz, $CDCl_3$) δ 140.7, 137.4, 131.3, 126.2, 124.6, 122.0, 121.5, 120.5, 114.3, 107.3, 87.2, 82.2, 59.8, 55.7, 53.0, 35.9, 34.9, 32.9, 28.7, 28.4, 27.5; IR (film): 2962, 2904, 2864, 1632, 1541, 1456 cm^{-1}; HRMS-ESI (*m/z*) $[M + H]^+$ calcd for $C_{21}H_{26}NO$, 308.20144; found 308.20022; $[\alpha]^{21.4}_D$ +115.40° (*c* = 1.000, $CHCl_3$).

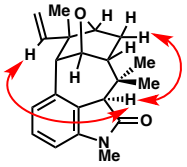


14 ***15***

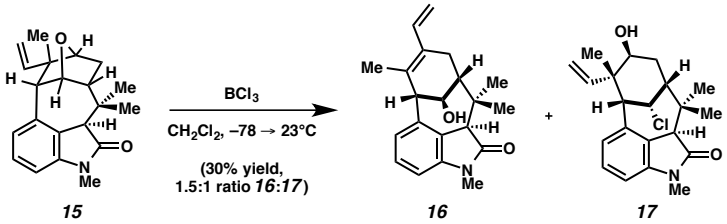
Oxindole 15. To a solution of indole **14** (137 mg, 0.44 mmol, 1.0 equiv) in CH_2Cl_2 (8.2 mL) at 0 ºC was added NBS (80.0 mg, 0.45 mmol, 1.01 equiv) in one portion. The reaction vial was flushed with N_2, and then allowed to stir at 0 ºC. After 15 min, solid $NaHCO_3$ (137 mg, 100 wt %) was added in one portion. The reaction was removed from the 0 ºC bath and allowed to stir at room temperature for 5 min. The resulting suspension was then concentrated under reduced pressure. Absolute ethanol (7.0 mL) and concentrated aqueous HCl (7.0 mL) were added. After heating to 80 ºC for 2 h, the reaction mixture was cooled to room temperature and transferred to a separatory funnel with H_2O (14 mL) and EtOAc (14 mL). To the separatory funnel was slowly added solid $NaHCO_3$ until gas evolution was no longer observed. The resulting biphasic mixture was extracted with EtOAc (3 x 14 mL) and the organic layers were combined, dried over Na_2SO_4, and evaporated under reduced pressure. The resulting residue was purified by flash chromatography (9:1 hexanes:EtOAc) to afford oxindole **15** (120 mg, 83% yield) as a white solid. Oxindole **15**: mp: 138.4 ºC; R_f 0.59 (1:1 hexanes:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.19 (ddd, *J* = 7.8, 7.8, 0.6, 1H), 6.76 (d, *J* = 7.5, 1H), 6.70 (d, *J* = 7.7, 1H), 5.53 (dd, *J* = 17.9, 11.2, 1H), 4.96 (dd, *J* = 11.2, 1.2, 1H), 4.84 (dd, *J* = 17.9, 1.2, 1H), 4.47 (app t, *J* = 5.0, 1H), 4.38 (d, *J* = 5.8, 1H), 3.46 (s, 1H), 3.19 (s, 3H), 3.02 (d, *J* = 4.5, 1H), 2.31–2.22 (m, 1H), 2.11 (dd, *J* = 12.9, 6.6, 1H), 1.98 (ddd, *J* = 12.2, 12.2, 5.8, 1H), 1.43 (s, 3H), 1.35 (s, 3H), 0.73 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$: δ 176.6, 144.2, 140.6, 134.3, 128.1, 126.5, 126.2, 116.4, 106.6, 87.0, 80.8, 60.3, 56.5, 51.2, 49.9, 37.0, 31.9, 27.8, 27.6, 26.3, 23.2; IR (film): 2962, 1703, 1605, 1469, 1324 cm^{-1}; HRMS-ESI

(*m/z*) $[M + H]^+$ calcd for $C_{21}H_{26}NO_2$, 324.19635; found 324.19514; $[\alpha]^{21.4}_D$ +28.20° (*c* = 1.000, $CHCl_3$).

The structure of **15** was confirmed by a 2D-NOESY experiment, as the following interactions were observed:



15

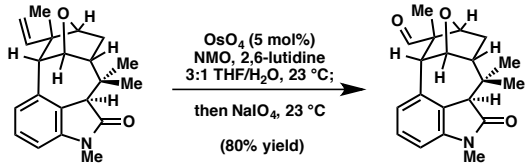


15 ***16*** ***17***

Diene 16 and Alkyl Chloride 17. A solution of oxindole **15** (6.1 mg, 0.019 mmol, 1.0 equiv) in CH_2Cl_2 (1.89 mL) was cooled to –78 °C. A solution of BCl_3 (1.0 M in CH_2Cl_2, 145.4 μL, 0.14 mmol, 7.7 equiv) was added in a dropwise manner. The resulting solution was allowed to stir at –78 °C. After 30 min, the solution was allowed to warm to 0 ºC. After 2 additional hours, the solution was warmed to room temperature. After 4 h, the reaction was quenched by the addition of a saturated aqueous solution of $NaHCO_3$ (1 mL), transferred to a separatory funnel with EtOAc (6 mL) and H_2O (4 mL), and extracted with EtOAc (3 x 3 mL). The organic layers were combined, dried over Na_2SO_4, and evaporated under reduced pressure. The resulting residue was purified by preparative thin layer chromatography (1:1 hexanes:EtOAc) to afford diene **16** (1.1 mg, 18% yield) and alkyl chloride **17** (0.8 mg, 12% yield) as amorphous solids. Diene **16**: R_f 0.60 (1:1 hexanes:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.21 (ddd, *J* = 7.8, 7.8, 0.6, 1H), 6.91 (d, *J* = 7.3, 1H), 6.76 (dd, *J* = 17.2, 11.0, 1H), 6.67 (d, *J* = 7.8, 1H), 5.32 (d, *J* = 17.2, 1H), 5.09 (d, *J* = 11.1, 1H), 4.24 (br. s, 1H), 3.32 (s, 1H), 3.25 (s, 1H), 3.14 (s, 3H), 2.73 (d, *J* = 18.7, 1H), 2.56 (dd, *J* = 18.7, 7.9, 1H), 2.02 (d, *J* = 7.9, 1H), 1.79 (d, *J* = 6.7, 1H), 1.68 (s, 3H), 1.54 (s, 3H), 0.73 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 176.4, 144.4, 135. 8, 134.0, 128.9, 128.1, 126.6, 126.4, 123.5, 112.9, 106.4, 67.5, 54.4, 50.9, 49.1, 39.0, 28.0, 26.1, 22.5, 21.2, 17.8; IR (film): 3412, 2969, 1690, 1608, 1470 cm^{-1}; HRMS-ESI (*m/z*) $[M + H]^+$ calcd for $C_{21}H_{26}NO_2$, 324.19635; found 324.19417; $[\alpha]^{21.4}_D$ –264.00° (*c* = 0.150, $CHCl_3$).

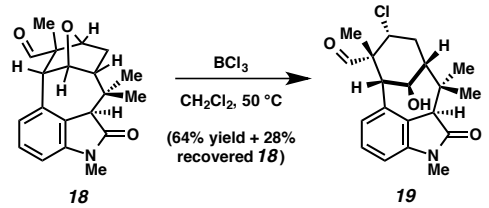
Alkyl chloride **17**: R_f 0.52 (1:1 hexanes:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$, 25 of 26 observed): δ 7.16 (ddd, *J* = 7.8, 7.8, 0.7, 1H), 6.68 (dd, *J* = 7.8, 0.7, 1H), 6.65 (d, *J* = 7.7, 1H), 5.31 (dd, *J* = 17.4, 10.7, 1H), 5.12 (dd, *J* = 17.4, 1.0, 1H), 5.03 (dd, *J* = 10.7, 1.0, 1H), 4.69 (br. s, 1H), 4.12 (dd, *J* = 10.3, 7.1, 1H), 3.57 (s, 1H), 3.20–3.18 (m, 1H), 3.17 (s, 3H), 2.37–2.32 (m, 2H), 2.28–2.25 (m, 1H), 1.67 (s, 3H), 1.57 (s, 3H), 0.89 (s, 3H);

^{13}C NMR (125 MHz, $CDCl_3$): δ 175.2, 146.3, 145.0, 138.7, 128.0, 126.8, 124.1, 114.8, 106.8, 69.7, 59.3, 58.2, 56.8, 54.8, 46.5, 39.4, 27.3, 26.3, 25.3, 23.3, 19.0; IR (film): 3451, 2962, 2872, 1699, 1609 cm^{-1}; HRMS-ESI (*m/z*) $[M + H]^+$ calcd for $C_{21}H_{27}ClNO_2$, 360.17303; found 360.17087; $[\alpha]^{21.2}_D$ –9.00° (*c* = 0.400, $CHCl_3$).



15 ***18***

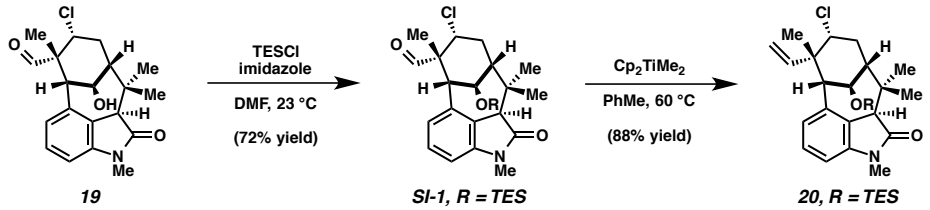
Aldehyde 18. To a solution of oxindole **15** (45 mg, 0.14 mmol, 1.0 equiv) in a 3:1 mixture of THF/H_2O (1.4 mL) was added 2,6-lutidine (32 μL, 0.28 mmol, 2.0 equiv), OsO_4 (20 mg/mL in H_2O, 84 μL, 0.007 mmol, 0.05 equiv), and NMO (65 mg, 0.56 mmol, 4.0 equiv). The vial was flushed with N_2, sealed and stirred at room temperature. After 19 h, solid $NaIO_4$ (89 mg, 0.42 mmol, 3.0 equiv) was added in one portion and the reaction mixture was stirred at room temperature. After 13 min, the reaction mixture was quenched with a saturated aqueous solution of $Na_2S_2O_3$ (1 mL) and stirred vigorously at room temperature. After 30 min the resulting mixture was transferred to a test tube with EtOAc (5 mL) and H_2O (5 mL). The resulting biphasic mixture was extracted with EtOAc (3 x 3 mL). The organic layers were combined, dried over Na_2SO_4, and evaporated under reduced pressure. The resulting residue was purified by preparative thin layer chromatography (3:1 hexanes:EtOAc) to afford aldehyde **18** (36 mg, 80% yield) as a white solid. Aldehyde **18**: mp: 181.1 ºC; R_f 0.53 (1:1 hexanes:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.17 (s, 1H), 7.24 (dd, *J* = 7.7, 7.7, 1H), 6.89 (d, *J* = 7.7, 1H), 6.74 (d, *J* = 7.8, 1H), 4.55 (t, *J* = 4.9, 1H), 4.47 (d, *J* = 5.0, 1H), 3.26 (s, 1H), 3.18–3.16 (m, 4H), 2.37–2.29 (m, 1H), 2.16–2.07 (m, 2H), 1.43 (s, 3H), 1.37 (s, 3H), 0.74 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 204.6, 175.9, 144.7, 131.8, 128.8, 125.65, 125.60, 107.4, 84.6, 81.0, 59.1, 58.9, 56.0, 49.3, 36.9, 282, 27.5, 26.4, 25.4, 23.2; IR (film): 2959, 2928, 1708, 1606, 1470 cm^{-1}; HRMS-ESI (*m/z*) $[M + H]^+$ calcd for $C_{20}H_{24}NO_3$, 326.17562; found 326.17443; $[\alpha]^{21.6}_D$ +23.80° (*c* = 1.000, $CHCl_3$).



18 ***19***

Alkyl Chloride 19. To a scintillation vial containing oxindole **18** (19.3 mg, 0.059 mmol, 1.0 equiv) was added a solution of BCl_3 (1.0 M in CH_2Cl_2, 178.2 μL, 0.178 mmol, 3.0 equiv) in a dropwise manner. The reaction vial was then sealed and heated to 50 °C. After 2 h, the solution was allowed to cool to 23 ºC, and quenched by the addition of a

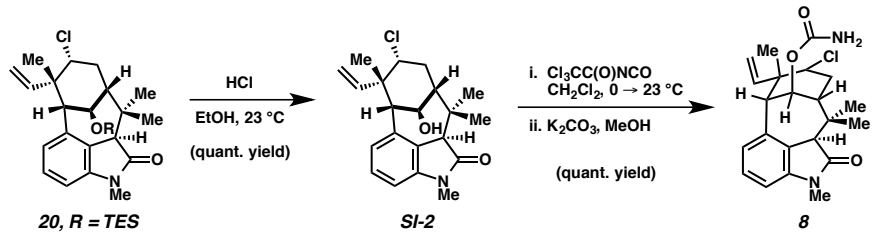
saturated aqueous solution of $NaHCO_3$ (1 mL), transferred to a separatory funnel with EtOAc (6 mL) and H_2O (6 mL), and extracted with EtOAc (3 x 3 mL). The organic layers were combined, dried over Na_2SO_4, and evaporated under reduced pressure. The resulting residue was purified by preparative thin layer chromatography (1:1 hexanes:EtOAc) to afford alkyl chloride **19** (13.7 mg, 64% yield) as a white solid and recovered oxindole **18** (5.4 mg, 28% yield). Alkyl chloride **19**: mp: 176.4 ºC; R_f 0.42 (1:1 hexanes:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.29 (s, 1H), 7.18 (dd, *J* = 7.7, 7.7, 1H), 6.75 (d, *J* = 7.7, 1H), 6.70 (d, *J* = 7.8, 1H), 5.13–5.04 (m, 1H), 4.18 (s, 1H), 3.47 (s, 1H), 3.24–3.21 (m, 1H), 3.16 (s, 3H), 2.61–2.56 (m, 2H), 2.20–2.16 (m, 1H) 1.90 (s, 1H), 1.58 (s, 3H), 1.56 (s, 3H), 0.88 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 200.3, 175.8, 144.9, 133.8, 128.9, 125.1, 124.8, 107.5, 69.6, 61.8, 57.4, 53.8, 51.6, 50.5, 39.5, 31.3, 26.4, 26.1, 25.9, 22.8; IR (film): 3443, 2967, 1689, 1609, 1594 cm^{-1}; HRMS-ESI (*m/z*) $[M + H]^+$ calcd for $C_{20}H_{25}ClNO_3$, 362.15230; found 362.15085; $[\alpha]^{23.0}_D$ +59.60° (*c* = 1.000, $CHCl_3$).



Silyl Ether 20. To a solution of **19** (18.8 mg, 0.052 mmol, 1.0 equiv) in DMF (944 μL) was added imidazole (35.3 mg, 0.52 mmol, 3.0 equiv). The reaction vial was then purged with N_2 and TESCl (26.2 μL, 0.156 mmol, 3.0 equiv) was added in a dropwise manner. The resulting solution was stirred at room temperature. After 1 h the reaction was quenched by the addition of a saturated aqueous solution of $NaHCO_3$ (2 mL) and transferred to a separatory funnel with EtOAc (6 mL) and H_2O (4 mL). After extracting with EtOAc (3 x 3 mL), the organic layers were combined, dried over Na_2SO_4, and evaporated under reduced pressure. The resulting residue was purified by preparative thin layer chromatography (1:1 hexanes:EtOAc) to afford **SI-1** (18 mg, 72% yield) as an amorphous solid. **SI-1**: R_f 0.69 (1:1 hexanes:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.30 (s, 1H), 7.18 (ddd, *J* = 7.8, 7.7, 0.65, 1H), 6.72 (d, *J* = 7.6, 1H), 6.70 (d, *J* = 7.8, 1H), 5.12–5.03 (m, 1H), 4.10–4.04 (m, 1H), 3.46 (s, 1H), 3.16 (s, 3H), 3.14–3.10 (m, 1H), 2.61–2.51 (m, 2H), 2.19–2.11 (m, 1H), 1.55 (s, 3H), 1.54 (s, 3H), 0.96 (t, *J* = 7.9, 9H), 0.86 (s, 3H), 0.59 (q, *J* = 7.9, 6H).

To a vial containing **SI-1** (17.9 mg, 0.038 mmol, 1.0 equiv) was added the Petasis reagent (1.0 M in PhMe, 444 μL, 0.444 mmol, 11.8 equiv) in the absence of light. The reaction vessel was then sealed and heated to 60 °C. After 4.5 h the reaction was cooled to room temperature and filtered by passage over a plug of silica gel (3:1 hexanes:EtOAc eluent, 15 mL). The filtrate was evaporated under reduced pressure and the resulting residue was purified by preparative thin layer chromatography (3:1 hexanes:EtOAc) to afford silyl ether **20** (15.6 mg, 88% yield) as an amorphous solid. Silyl Ether **20**: R_f 0.57 (3:1 hexanes:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.14 (dd, *J* = 7.7, 7.7, 1H), 6.65 (d, *J* = 7.6, 1H), 6.62 (d, *J* = 7.6, 1H), 5.65 (dd, *J* = 17.2, 10.9, 1H), 5.15 (dd, *J* = 12.7, 4.5,

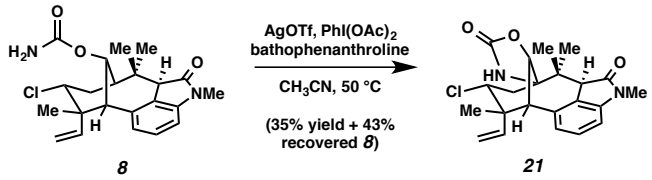
1H), 4.85 (dd, *J* = 17.3, 0.9, 1H), 4.80 (d, *J* = 11.1, 1H), 4.04 (br. s, 1H), 3.46 (s, 1H), 3.17 (s, 3H), 3.12–3.08 (m, 1H), 2.43–2.34 (m, 1H), 2.19–2.03 (m, 2H), 1.51 (s, 3H), 1.50 (s, 3H), 0.96 (t, *J* = 7.9, 9H), 0.85 (s, 3H), 0.58 (q, *J* = 7.8, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 176.2, 144.5, 138.6, 138.3, 128.0, 125.5, 124.4, 115.0, 106.3, 70.0, 65.3, 60.7, 54.8, 50.6, 44.4, 39.7, 31.5, 29.7, 26.3, 25.9, 22.6, 7.1, 4.9; IR (film): 2956, 2912, 1708, 1610, 1597 cm^{-1}; HRMS-ESI (*m/z*) $[M + H]^+$ calcd for $C_{27}H_{41}ClNO_2Si$, 474.25951; found 474.25746; $[\alpha]^{21.0}_D$ –1.40° (*c* = 1.000, $CHCl_3$).



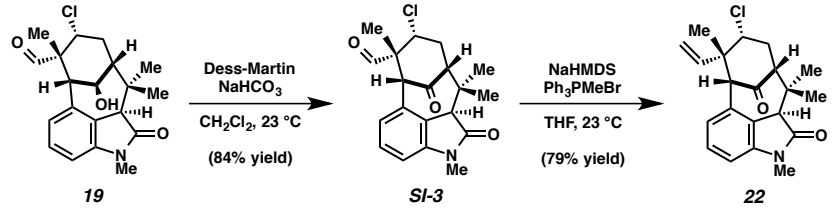
Carbamate 8. To a flask containing silyl ether **20** (5.4 mg, 0.011 mmol, 1.0 equiv), was added absolute ethanol (542 μL) and concentrated aqueous HCl (542 μL). The solution was then allowed to stir at room temperature. After 20 min, the reaction mixture was transferred to a separatory funnel with EtOAc (6 mL). To the funnel was slowly added a saturated aqueous solution of $NaHCO_3$ (5 mL) until gas evolution was no longer observed. The resulting biphasic mixture was extracted with EtOAc (3 x 3 mL) and the organic layers were combined, dried over Na_2SO_4, and evaporated under reduced pressure. The resulting residue was purified by preparative thin layer chromatography (1:1 hexanes:EtOAc) to afford **SI-2** (4.1 mg, quant. yield) as an amorphous solid. **SI-2**: R_f 0.18 (3:1 hexanes:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.14 (dd, *J* = 7.7, 7.7, 1H), 6.67–6.63 (m, 2H), 5.64 (dd, *J* = 17.3, 11.0, 1H), 5.14 (dd, *J* = 12.8, 4.5, 1H), 4.87 (dd, *J* = 17.2, 0.8, 1H), 4.81 (d, *J* = 11.1, 1H), 4.15 (s, 1H), 3.47 (s, 1H), 3.17 (s, 3H), 2.42 (ddd, *J* = 14.7, 10.8, 5.3,1H), 2.21–2.07 (m, 2H), 1.54 (s, 3H), 1.52 (s, 3H), 0.85 (s, 3H).

To a solution of **SI-2** (4.1 mg, 0.011 mmol, 1.0 equiv) in CH_2Cl_2 (228 μL) at 0 °C was added trichloroacetyl isocyanate (1.7 μL, 0.0142 mmol, 1.25 equiv) in a dropwise manner. The resulting mixture was allowed to stir at 0 °C for 5 min, and then at room temperature for 30 min. The solvent was evaporated under reduced pressure. To the resulting residue was added MeOH (228 μL), followed by K_2CO_3 (8.6 mg, 0.0626 mmol, 5.5 equiv) in one portion. The vial was flushed with N_2 and left to stir at room temperature. After 1 h, the reaction was quenched with a saturated aqueous solution of NH_4Cl (1 mL), and the resulting biphasic mixture was transferred to a separatory funnel with EtOAc (6 mL) and H_2O (4 mL). After extracting with EtOAc (3 x 3 mL), the organic layers were combined, dried over Na_2SO_4, and evaporated under reduced pressure. The resulting residue was purified by preparative thin layer chromatography (1:1 hexanes:EtOAc) to afford carbamate **8** (4.6 mg, quant. yield) as an amorphous solid. Carbamate **8**: R_f 0.44 (1:1 hexanes:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.15 (dd, *J* = 7.8, 7.8, 1H), 6.70–6.63 (m, 2H), 5.62 (dd, *J* = 17.2, 10.8, 1H), 5.14–5.09 (m, 1H), 4.88 (dd, *J* = 17.2, 0.7, 1H), 4.84 (d, *J* = 11.0, 1H), 4.77 (dd, *J* = 12.7, 4.7, 1H), 4.66 (s, 2H), 3.47 (s, 1H), 3.28–3.25 (m, 1H), 3.18 (s, 3H), 2.44–2.34 (m, 1H), 2.23–2.13 (m, 2H),

1.53, (s, 3H), 1.50 (s, 3H), 0.93 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 175.9, 155.3, 144.5, 137.9, 137.0, 128.2, 125.7, 124.4, 115.6, 106.7, 73.2, 64.6, 57.0, 51.1, 50.7, 44.1, 39.7, 31.0, 29.4, 26.4, 25.7, 22.3; IR (film): 3489, 3348, 2966, 1694, 1610 cm^{-1}; HRMS-ESI (*m/z*) [M + H]$^+$ calcd for $C_{22}H_{28}ClN_2O_3$, 403.17885; found 403.17618; $[\alpha]^{23.4}_D$ – 89.33° (*c* = 1.000, $CHCl_3$).

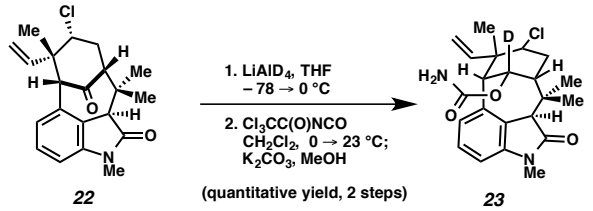


Oxazolidinone 21. A 1-dram vial containing CH_3CN, a second 1-dram vial charged with bathophenanthroline (3.8 mg, 0.011 mmol, 1.0 equiv), and a third 1-dram vial containing carbamate **8** (4.6 mg, 0.011 mmol, 1.0 equiv) and $PhI(OAc)_2$ (14.7 mg, 0.046 mmol, 4.0 equiv) were transferred into the glovebox. AgOTf (2.9 mg, 0.011 mmol, 1.0 equiv) and CH_3CN (200 μL) were added to the vial containing the bathophenanthroline, and the resulting suspension was allowed to stir at room temperature for 20 min. Next, CH_3CN (126 μL) was added to the vial containing the carbamate, and the AgOTf/bathophenanthroline suspension was also added to this vial. The vial was then sealed, removed from the glovebox, and the resulting mixture was heated to 50 °C. After 20.5 h, the reaction was cooled to room temperature and filtered by passage over a plug of celite (EtOAc eluent, 10 mL). The filtrate was evaporated under reduced pressure, and the resulting residue was purified by preparative thin layer chromatography (1:2:2 PhH:CH_2Cl_2:Et_2O) to afford oxazolidinone **21** (1.6 mg, 35% yield) as an amorphous solid and recovered carbamate **8** (2.0 mg, 43% yield). Oxazolidinone **21**: R_f 0.43 (1:2:2 PhH:Et_2O:CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.21 (dd, *J* = 7.8, 7.8, 1H), 6.75–6.68 (m, 2H), 5.77 (s, 1H), 5.39 (dd, *J* = 17.1, 10.8, 1H), 5.02 (d, *J* = 17.2, 1H), 4.94 (d, *J* = 10.8, 1H) 4.71 (d, *J* = 2.0, 1H), 4.62 (dd, *J* = 13.7, 3.6, 1H), 3.59 (s, 1H), 3.46 (s, 1H), 3.20 (s, 3H), 2.67 (app t, *J* = 14.3, 1H), 2.19 (dd, *J* = 14.7, 3.6, 1H), 1.61 (s, 3H), 1.58 (s, 3H), 0.95 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 174.2, 158.0, 144.7, 137.9, 136.4, 128.7, 126.7, 123.0, 116.0, 107.3, 78.7, 67.5, 61.7, 53.6, 52.7, 44.4, 41.3, 40.2, 28.3, 26.5, 21.1, 17.8; IR (film): 3268, 2975, 1754, 1702, 1610 cm^{-1}; HRMS-ESI (*m/z*) [M + H]$^+$ calcd for $C_{22}H_{26}ClN_2O_3$, 401.16320; found 401.16188; $[\alpha]^{20.5}_D$ +68.60° (*c* = 1.000, $CHCl_3$).



Ketone 22. To a flask containing alkyl chloride **19** (15.1 mg, 0.042 mmol, 1.0 equiv) was added solid $NaHCO_3$ (17.5 mg, 0.054 mmol, 5.0 equiv) in one portion. The reaction vessel was flushed with N_2, and then CH_2Cl_2 (834 μL) was added. To the resulting suspension was added the Dess–Martin periodinane reagent (23.0 mg, 0.21 mmol, 1.3 equiv) in one portion. The flask was flushed with N_2, and the reaction mixture was allowed to stir at room temperature. After 1 h, the reaction mixture was diluted with a 1:1 mixture of saturated aqueous $NaHCO_3$ and saturated aqueous $Na_2S_2O_3$ (1.0 mL). The resulting biphasic mixture was vigorously stirred until both layers appeared clear. The mixture was then transferred to a separatory funnel with EtOAc (6 mL) and H_2O (4 mL), and then extracted with EtOAc (3 x 3 mL). The organic layers were combined, dried over Na_2SO_4, and evaporated under reduced pressure. The resulting residue was purified by preparative thin layer chromatography (1:1 hexanes:EtOAc) to afford **SI-3** (12.6 mg, 84% yield) as a white foam. **SI-3**: R_f 0.88 (1:3 hexanes:EtOAc); ^{1}H NMR (500 MHz, C_6D_6): δ 9.06 (d, *J* = 1.2, 1H), 6.76 (ddd, *J* = 7.8, 7.8, 0.8, 1H), 6.33 (d, *J* = 7.6, 1H), 6.00 (d, *J* = 7.5, 1H), 3.41 (d, *J* = 2.2, 1H), 3.40 (s, 1H), 3.35 (ddd, *J* = 13.5, 4.5, 0.9, 1H), 2.84 (m, 1H), 2.52 (s, 3H), 2.28–2.21 (m, 1H), 1.93 (ddd, *J* = 14.6, 10.7, 4.6, 1H), 1.40 (s, 3H), 1.13 (s, 3H), 0.70 (s, 3H).

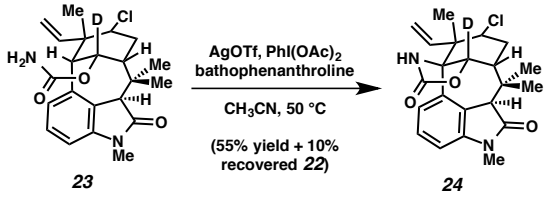
To a vial containing methyl triphenylphosphonium bromide (373 mg, 1.04 mmol, 15.0 equiv) was added THF (1.7 mL). The reaction vessel was cooled to 0 °C and NaHMDS (1.0 M in THF, 836 μL, 0.84 mmol, 12.0 equiv) was added in a dropwise manner. The vial was allowed to warm to room temperature and left to stir for 20 min. A solution of **SI-3** (25.0 mg, 0.070 mmol, 1.0 equiv) in THF (2.4 mL) was added dropwise in three portions and the reaction was left to stir at room temperature. After 30 min, the reaction was quenched by the the addition of a saturated aqueous solution of NH_4Cl (5 mL). The resulting biphasic mixture was transferred to a separatory funnel with EtOAc (15 mL) and H_2O (10 mL). After extracting with EtOAc (3 x 15 mL), the organic layers were combined, dried over $MgSO_4$, and evaporated under reduced pressure. The resulting crude mixture was filtered by passage over a plug of silica gel (1:1 hexanes:EtOAc, 40 mL). The filtrate was evaporated under reduced pressure and the resulting residue was purified by flash chromatography (7:1 hexanes:EtOAc) to afford ketone **22** (77.4 mg, 79% yield) as a white solid. Ketone **22**: mp: 110.4 ºC; R_f 0.67 (1:1 hexanes:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.21 (dd, *J* = 7.7, 7.7, 1H), 6.70 (d, *J* = 7.6, 1H), 6.68 (d, *J* = 7.7, 1H), 5.82 (dd, *J* = 17.4, 11.1, 1H), 5.00–4.95 (m, 2H), 3.99 (dd, *J* = 12.1, 3.6, 1H), 3.72 (s, 1H), 3.61 (d, *J* = 2.0, 1H), 3.19 (s, 3H), 2.75–2.64 (m, 2H), 2.54–2.47 (m, 1H), 1.55 (s, 3H), 1.48 (s, 3H), 0.71 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 207.6, 175.3, 144.6, 136.2, 132.1, 129.0, 125.2, 124.4, 117.9, 107.3, 68.9, 64.5, 62.5, 50.9, 48.6, 41.8, 32.6, 29.7, 26.5, 25.0, 22.2; IR (film): 1702, 1607, 1591, 1465 cm^{-1}; HRMS-ESI (*m/z*) [M + H]$^+$ calcd for $C_{21}H_{25}ClNO_2$, 358.15738; found 358.15590; $[\alpha]^{23.4}_D$ +12.0° (*c* = 1.000, $CHCl_3$).



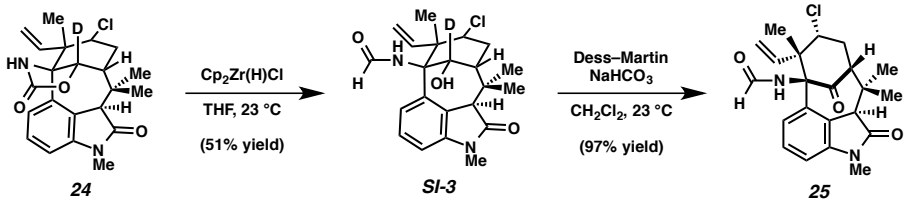
22 ***23***

Carbamate 23. To a solution of ketone **22** (87 mg, 0.244 mmol, 1.0 equiv) in THF (24.4 mL) at –78 °C was added a solution of $LiAlD_4$ (1.0 M in THF, 731 μL, 0.731 mmol, 3.0 equiv) in a dropwise manner. After stirring at –78 °C for 10 min, the solution was then allowed to warm to 0 ºC. After 12 min, the reaction was quenched at 0 °C by the slow addition of a saturated solution of aqueous Rochelle's salt (10 mL), and then allowed to warm to 23 ºC. The resulting biphasic mixture was stirred at room temperature for 1 h, transferred to a separatory funnel with EtOAc (10 mL) and H_2O (10 mL), and extracted with EtOAc (3 x 10 mL). The organic layers were combined, dried over $MgSO_4$, and evaporated under reduced pressure. The resulting residue was used in the subsequent step without further purification.

To a flask containing the crude residue from the previous step was added CH_2Cl_2 (4.9 mL). The reaction vessel was cooled to 0 ºC and trichloroacetyl isocyanate (36.3 μL, 0.305 mmol, 1.25 equiv) was added in a dropwise manner. The resulting mixture was allowed to stir at 0 °C for 5 min, and then at room temperature for 20 min. The solvent was evaporated under reduced pressure. To the resulting residue was added MeOH (4.9 mL) and solid K_2CO_3 (185 mg, 1.34 mmol, 5.5 equiv) in one portion. The reaction was flushed with N_2 and left to stir at room temperature for 1 h. The reaction was quenched by the addition of a solution of saturated aqueous NH_4Cl (5.0 mL), and the resulting biphasic mixture was transferred to a separatory funnel with EtOAc (10 mL) and H_2O (10 mL). After extracting with EtOAc (3 x 10 mL), the organic layers were combined, dried over $MgSO_4$, and evaporated under reduced pressure. The resulting residue was purified by flash chromatography (2:1 → 1:1 hexanes:EtOAc) to afford carbamate **23** (98 mg, quantitative yield, over two steps) as a white solid. Carbamate **23**: mp: 102.8 ºC; R_f 0.56 (2:1 EtOAc:hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.14 (dd, J = 7.7, 7.7, 1H), 6.68 (d, J = 7.6, 1H), 6.61 (d, J = 7.7, 1H), 5.72 (dd, J = 17.1, 10.9, 1H), 4.87–4.84 (m, 2H), 4.47–4.4 (m, 3H), 3.69 (s, 1H), 3.19 (s, 3H), 3.14 (s, 1H), 2.54–2.46 (m, 2H), 2.39–2.29 (m, 1H), 1.51 (s, 3H), 1.45 (s, 3H), 0.90 (s, 3H); ^{2}H NMR (77 MHz, $CDCl_3$) δ 5.43 (br. s, 1D); ^{13}C NMR (125 MHz, $CDCl_3$): δ 176.3, 155.8, 144.3, 137.9, 137.5, 127.8, 126.5, 125.3, 116.1, 106.6, 64.1, 56.1, 51.5, 46.6, 46.3, 39.1, 33.0, 29.0, 26.7, 26.4, 24.0; IR (film): 1724, 1701, 1607, 1467, 1376, cm^{-1}; HRMS-ESI (m/z) [M + H]$^+$ calcd for $C_{22}H_{27}DClN_2O_3$, 404.18512; found 404.18342; $[\alpha]^{24.3}_D$ –3.20° (c = 1.000, $CHCl_3$).



Oxazolidinone 24. A 1-dram vial containing CH_3CN, a second 1-dram vial charged with bathophenanthroline (13 mg, 0.039 mmol, 1.0 equiv), and a third 1-dram vial containing carbamate **23** (15.8 mg, 0.039 mmol, 1.0 equiv) and $PhI(OAc)_2$ (50 mg, 0.157 mmol, 4.0 equiv) were transferred into the glovebox. AgOTf (10 mg, 0.039 mmol, 1.0 equiv) and CH_3CN (550 μL) were added to the vial containing the bathophenanthroline, and the resulting suspension was allowed to stir at room temperature for 20 min. Next, CH_3CN (550 μL) was added to the vial containing the carbamate, and the AgOTf/bathophenanthroline suspension was also added to this vial. The vial was then sealed, removed from the glovebox, and the resulting mixture was heated to 50 °C. After 24 h, the reaction was cooled to room temperature and filtered by passage over a plug of silica gel (EtOAc eluent, 10 mL). The filtrate was evaporated under reduced pressure, and the resulting residue was purified by preparative thin layer chromatography (2:1:1 benzene:Et_2O:CH_2Cl_2) to afford oxazolidinone **24** (8.7 mg, 55% yield) as a white solid and recovered ketone **22** (1 mg, 10% yield). Oxazolidinone **24**: mp: 183.2 ºC; R_f 0.32 (1:2:2 benzene:Et_2O:CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.76 (s, 1H), 7.09 (dd, J = 7.9, 7.9, 1H), 6.69 (d, J = 7.8, 1H), 6.66 (d, J = 8.2, 1H), 5.54 (dd, J = 17.3, 10.7, 1H), 5.06 (d, J = 17.3, 1H), 5.00 (d, J = 10.9, 1H), 4.38–4.32 (m, 1H), 3.97 (s, 1H), 3.21 (s, 3H), 2.71–2.60 (m, 2H), 2.55–2.45 (m, 1H), 1.57 (s, 3H), 1.52 (s, 3H), 1.11 (s, 3H); ^{2}H NMR (77 MHz, $CDCl_3$) δ 4.91 (br. s, 1D); ^{13}C NMR (125 MHz, $CDCl_3$): δ 175.1, 159.5, 143.6, 138.7, 137.5, 128.2, 125.3, 124.1, 115.9, 107.0, 70.3, 63.1, 53.3, 47.9, 45.5, 38.2, 32.3, 27.1, 26.4, 23.3, 21.0; IR (film): 1748, 1703, 1683, 1610, 1591 cm^{-1}; HRMS-ESI (m/z) $[M + H]^+$ calcd for $C_{22}H_{25}DClN_2O_3$, 402.16947; found 402.16849; $[\alpha]^{23.1}_D$ +8.20° (c = 1.000, $CHCl_3$).

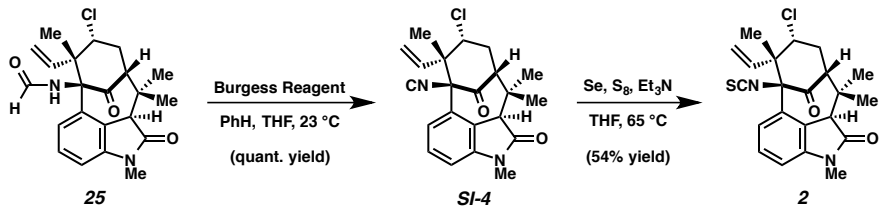


Formamide 25. Two 1-dram vials were charged with **24** (7.0 mg, 0.017 mmol, 1.0 equiv each) and taken into the glovebox. Each reaction vessel was charged with Schwartz' reagent (5.9 mg, 0.023 mmol, 1.3 equiv each) and THF (1.74 mL each), the latter of which had previously been taken through six freeze-pump-thaw cycles. The reaction vessels were sealed and left to stir at room temperature. After 14 h, the reaction vials were removed from the glovebox and quenched with a saturated aqueous solution of NH_4Cl (1 mL for each vial). The resulting biphasic mixtures were transferred to a test tube with EtOAc (2 mL) and brine (1 mL). After extracting with EtOAc (3 x 2 mL). The

organic layers were combined, dried over $MgSO_4$, and evaporated under reduced pressure. The resulting residue was purified by preparative thin layer chromatography (1:1 hexanes:acetone) to afford **SI-3**[5] (7.2 mg, 51% yield) as a white solid and recovered oxazolidinone **24** (3.1 mg, 22% yield). **SI-3**: R_f 0.09 (1:1 hexanes:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$):[6] 8.3–8.25 (m, 1.36H), 7.95 (s, 0.47H), 7.31–7.27 (m, 1.25H), 6.96 (d, *J* = 8.2, 0.41H), 6.87 (d, *J* = 8.1, 1H), 6.78-6.73 (m, *J* = 8.3, 2.0H), 6.22 (s, 1H), 6.10 (d, *J* = 11.2, 0.41H), 5.92 (dd, *J* = 17.8, 11.4, 1H), 5.88-5.80 (m, 0.87H), 5.05–4.97 (m, 0.8H), 4.94–4.85 (m, 3H), 4.79 (dd, *J* = 9.9, 5.5, 1H), 4.48 (dd, *J* = 9.2, 5.2, 0.5H), 4.33 (d, *J* = 8.2, 5.7, 0.38H), 4.20 (s, 0.36H), 4.10 (s, 0.38H), 4.06 (s, 1H), 3.23–3.19 (m, 5.7H), 2.73–2.49 (m, 4.5H), 2.44–2.36 (m, 1.5H), 1.57 (s, 3H), 1.56 (s, 3.5H), 1.52 (s, 4.4H), 1.50 (s, 1.71H), 1.23 (s, 1.34H), 1.18 (s, 3H), 0.95 (s, 1.4H).

A 1-dram vial was charged with **SI-3** (5.2 mg, 0.013 mmol, 1.0 equiv) and solid $NaHCO_3$ (5.4 mg, 0.065 mmol, 5.0 equiv) in one portion. The reaction vessel was flushed with N_2, and then CH_2Cl_2 (260 μL) was added. To the resulting suspension was added the Dess–Martin periodinane reagent (7.1 mg, 0.017 mmol, 1.3 equiv) in one portion. The flask was flushed with N_2, and the reaction mixture was allowed to stir at room temperature. After 1 h, the reaction mixture was diluted with a 1:1 mixture of saturated aqueous $NaHCO_3$ and saturated aqueous $Na_2S_2O_3$ (1.0 mL). The resulting biphasic mixture was vigorously stirred until both layers appeared clear. The mixture was then transferred to a test tube with EtOAc (2 mL) and brine (2 mL), and then extracted with EtOAc (3 x 2 mL). The organic layers were combined, dried over $MgSO_4$, and evaporated under reduced pressure. The resulting residue was purified by flash chromatography (5:1 → 3:1 hexanes:acetone) to afford formamide **25** (5.0 mg, 97% yield) as a white solid. formamide **25**: mp: 213.3 ºC; R_f 0.41 (3:1 EtOAc:hexanes); ^{1}H NMR (500 MHz, $CDCl_3$ at –44 °C):[7] δ 8.21 (d, *J* = 1.1, 0.25H), 7.53 (d, *J* = 12.0, 1H), 7.32 (dd, *J* = 8.1, 7.9, 1.25H), 7.02 (d, *J* = 8.1, 1H), 7.00 (d, *J* = 8.3, 0.25H), 6.82 (d, *J* = 7.5, 1H), 6.79 (d, *J* = 7.5, 0.25H), 6.38 (dd, *J* = 17.3, 11.0, 0.25H), 6.28 (dd, *J* = 17.3, 10.7, 1H), 5.78 (s, 0.25H), 5.73 (d, *J* = 11.5, 1H), 5.51 (d, *J* = 11.2, 0.25H), 5.48 (d, *J* = 11.0, 1H), 5.42–5.30 (m, 1.25H), 4.40 (s, 1H), 4.32 (s, 0.25H), 4.24 (d, *J* = 7.4, 1H), 4.19 (d, *J* = 7.1, 0.25H), 3.22 (s, 3H), 3.21 (s, 0.75H), 3.20–3.14 (m, 1H), 3.08–2.90 (m, 2.6H), 2.81 (d, *J* = 17.4, 1H), 2.75 (d, *J* = 16.4, 0.25H), 1.68 (s, 3H), 1.63 (s, 0.75H), 1.28 (s, 3.75H), 0.98 (s, 0.75H), 0.87 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 202.8, 174.3, 167.3, 144.0, 137.2, 133.7, 128.4, 126.7, 124.8, 118.2, 108.1, 71.5, 62.2, 60.2, 55.0, 49.8, 38.2, 31.8, 26.3, 26.1, 22.9, 20.9; IR (film): 2967, 2932, 1696, 1609, 1585 cm^{-1}; HRMS-ESI (*m/z*) $[M + H]^+$ calcd for $C_2H_{26}ClN_2O_3$, 401.16320; found 401.16143; $[\alpha]^{22.4}_D$ +9.60° (*c* = 1.000, $CHCl_3$).

[5] In our studies, products containing a formamide often assume a mixture of rotamers by ^{1}H NMR.
[6] **SI-3** was obtained as a 2.8:1.3:1 mixture of rotamers. These data represent empirically observed chemical shifts and coupling constants from the ^{1}H NMR spectrum.
[7] Formamide **25** was obtained as a 4:1 mixture of rotamers. These data represent empirically observed chemical shifts and coupling constants from the ^{1}H NMR spectrum.

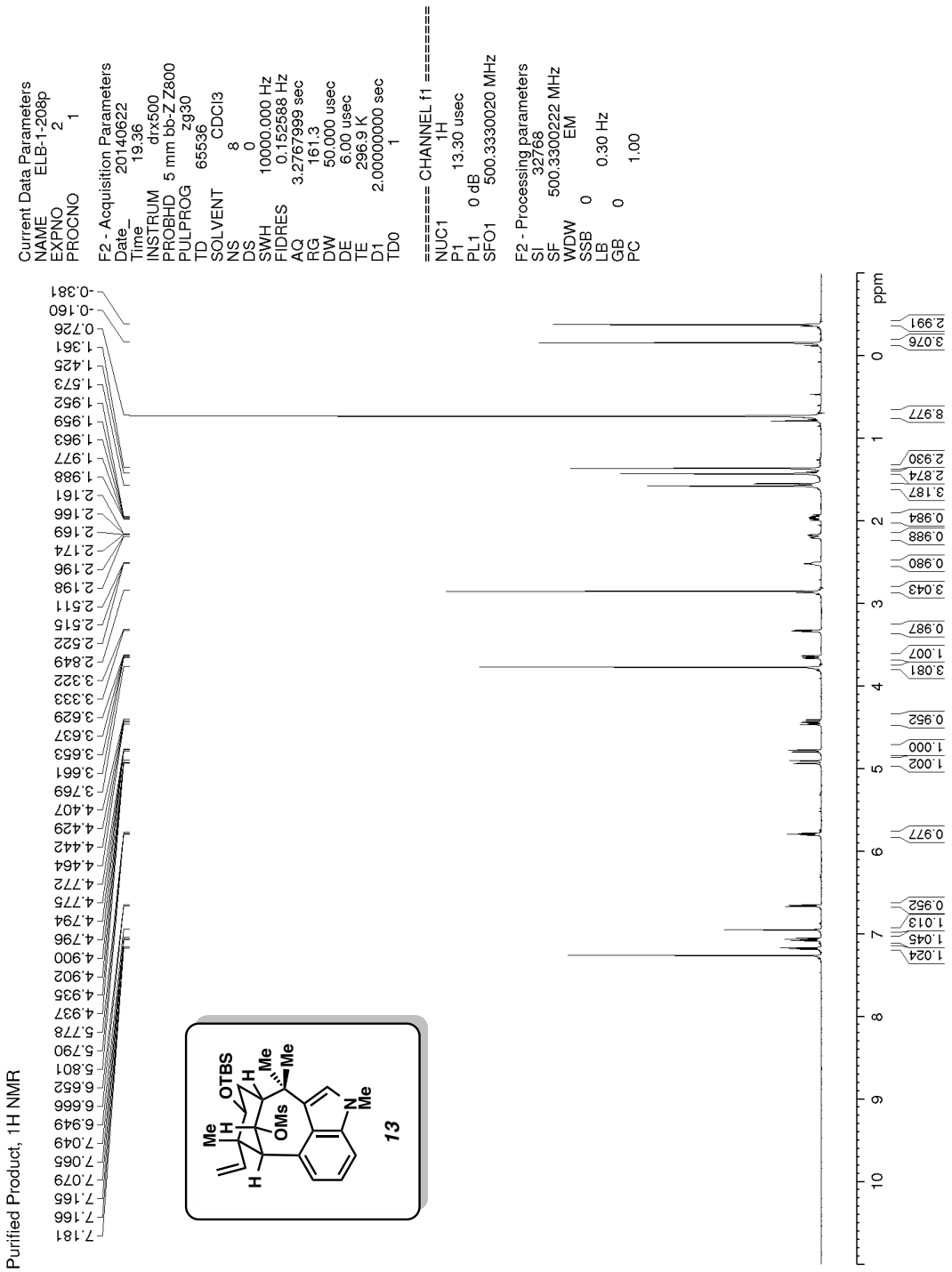


(–)-*N*-Methylwelwitindolinone B Isothiocyanate (2). To a solution of formamide **25** (3.3 mg, 0.008 mmol, 1.0 equiv) in 1:1 THF/PhH (660 μL) was added Burgess reagent (2.0 mg, 0.008 mmol, 1.0 equiv). The reaction vessel was purged with N_2, and then sealed and left to stir at room temperature. After stirring for 1 h, an additional portion of Burgess reagent (0.5 mg, 0.002 mmol, 0.25 equiv) was added. After stirring at room temperature for 30 min, a final portion of Burgess reagent (0.5 mg, 0.002 mmol, 0.25 equiv) was added and the resulting solution was stirred at room temperature. After 25 min, the reaction was filtered by passage over a plug of silica gel (EtOAc eluent, 6 mL). The filtrate was evaporated under reduced pressure and the resulting residue was purified by flash chromatography (5:1:1 hexanes:Et_2O:CH_2Cl_2) to afford **SI-4** (3.2 mg, quant. yield) as a white solid. **SI-4**: R_f 0.55 (1:1:1 hexanes:Et_2O:CH_2Cl_2); ^{1}H NMR (500 MHz, C_6D_6): δ 7.41 (d, *J* = 8.3, 1H), 6.86 (dd, *J* = 8.0, 8.0, 1H), 6.04 (d, *J* = 7.7, 1H), 5.82 (dd, *J* = 17.2, 11.0, 1H), 4.95–4.81 (m, 2H), 3.83 (s, 1H), 3.43 (dd, *J* = 6.4, 6.2, 1H), 2.55 (s, 3H), 2.36 (dd, *J* = 9.9, 3.6, 1H), 2.19–2.11 (m, 1H), 1.91–1.81 (m, 1H), 1.46 (s 3H), 1.26 (s, 3H), 0.75 (s, 3H).

Two 1-dram vials containing **SI-4** (2.9 mg, 0.008 mmol, 1.0 equiv each) were charged with powdered Se (1.8 mg, 0.023 mmol, 3.0 equiv each) and S_8 (1.9 mg, 0.590 mmol, 76.4 equiv each). The reaction vessels were purged with N_2 and to each vessel was added THF (584 μL, previously sparged with N_2 for 20 min) and NEt_3 (81 μL, 0.590 mmol, 26.4 equiv). Each reaction vessel was then sealed and heated to 65 °C. After 17 h, the reaction vials were cooled to room temperature. Their contents were combined and filtered by passage over a plug of silica gel (EtOAc eluent, 6 mL). The filtrate was evaporated under reduced pressure and the resulting residue was purified by preparative thin layer chromatography (1:1:1 hexanes:Et_2O:CH_2Cl_2) to afford (–)-**2** (3.4 mg, 54% yield) as a white solid. (–)-*N*-Methylwelwitindolinone B isothiocyanate (**2**): mp: 186.4 ºC; R_f 0.61 (1:1 hexanes:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34 (ddd, *J* = 8.3, 0.8, 1H), 7.25 (dd, *J* = 8.3, 0.9, 1H), 6.80 (d, *J* = 7.7, 1H), 5.99 (dd, *J* = 17.5, 11.1, 1H), 5.22–5.15 (m, 2H), 4.17 (app t, *J* = 6.3, 1H), 4.13 (s, 1H), 3.20 (s, 3H), 2.95 (app t, *J* = 7.2, 1H), 2.78 (app t, *J* = 6.5, 1H), 1.62 (s 3H), 1.48 (s, 3H), 0.83 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 198.6, 174.3, 144.1, 139.6, 136.4, 131.2, 128.8, 123.9, 122.6, 118.1, 108.3, 83.5, 62.5, 60.2, 53.3, 52.9, 39.8, 31.5, 26.4, 25.4, 24.1, 22.5; IR (film): 2969, 2933, 2049, 1710, 1607, 1587, 1460 cm^{-1}; HRMS-ESI (*m/z*) $[M + H]^+$ calcd for $C_{22}H_{24}ClN_2O_2S$, 415.12470; found 415.12245; $[\alpha]^{20.9}_D$ –133.71° (*c* = 0.071, CH_2Cl_2).[8]

[8] Reported values for specific rotations can be highly variable, for a pertinent discussion, see: Gawley, R. E. *J. Org. Chem.* **2006**, *71*, 2411–2416.

^{1}H and ^{2}H NMR Spectra: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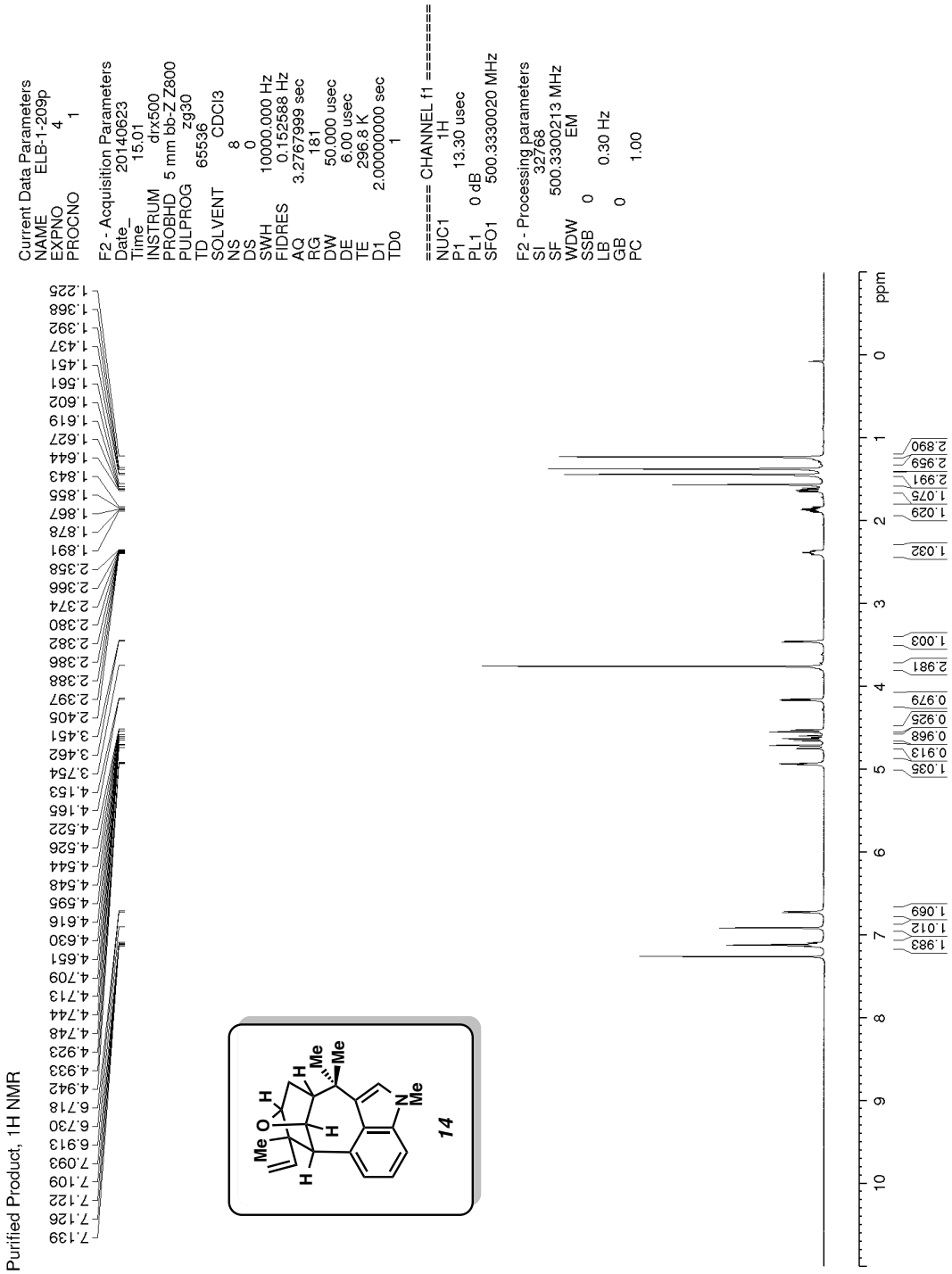
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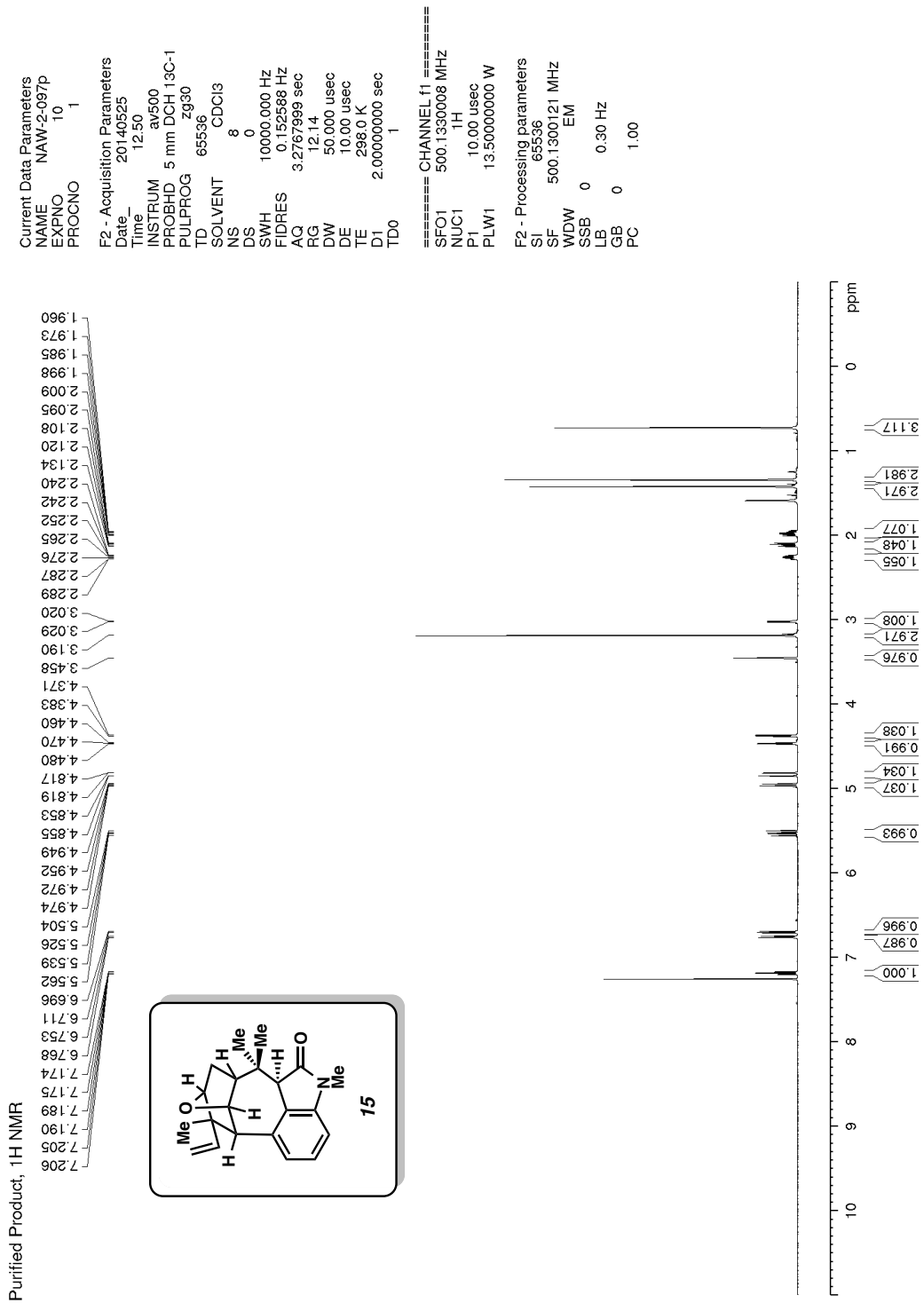
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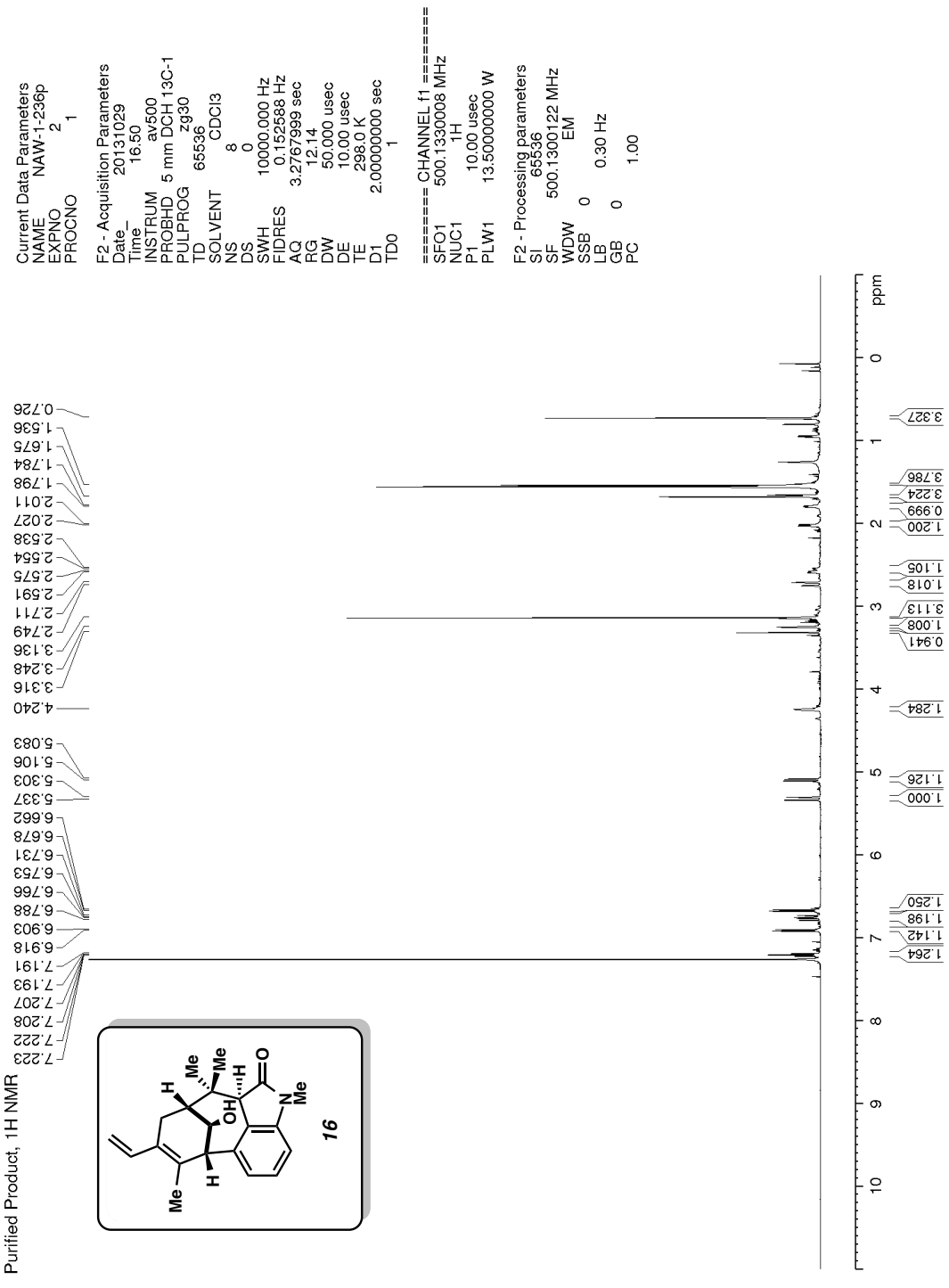
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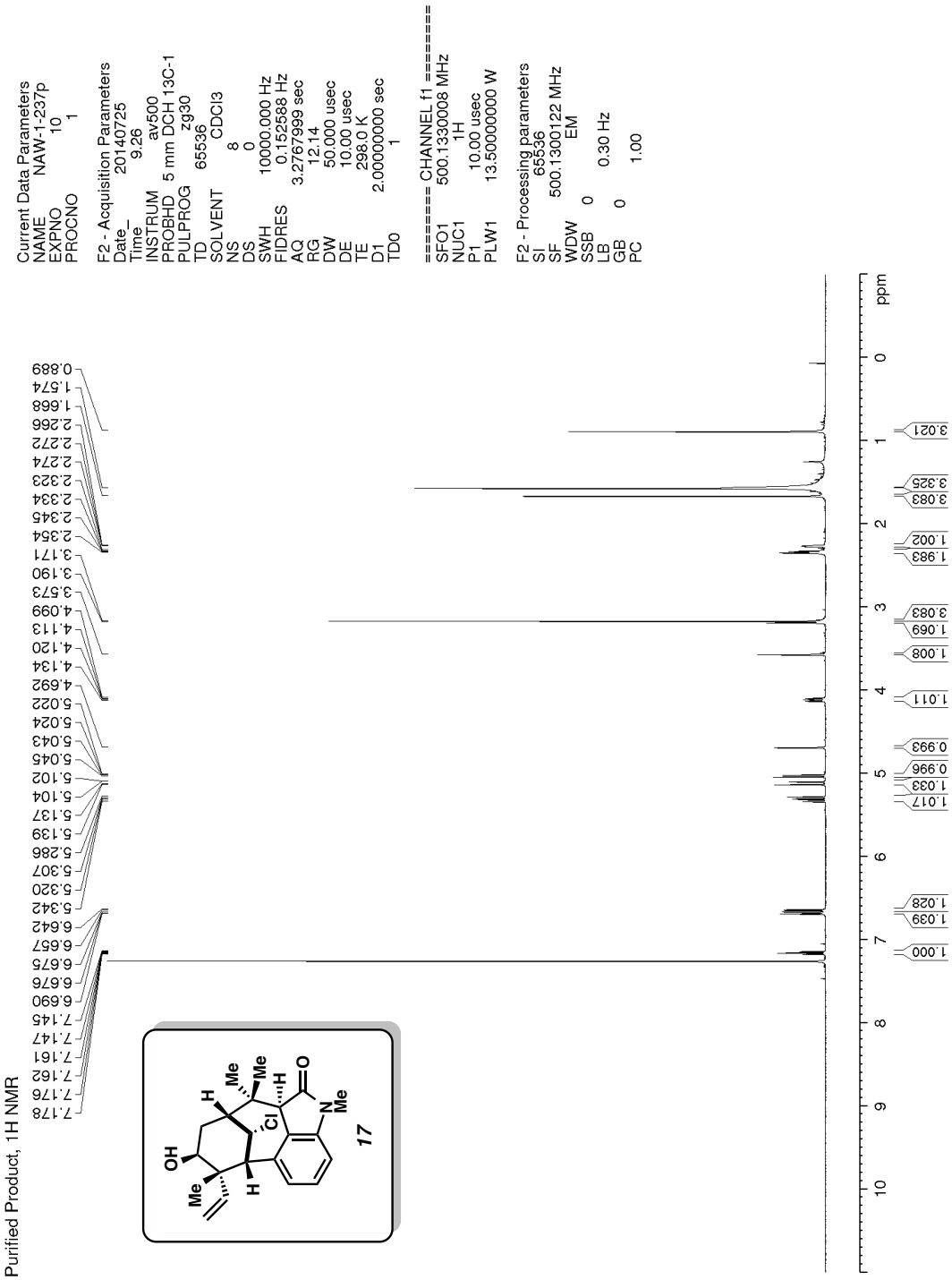
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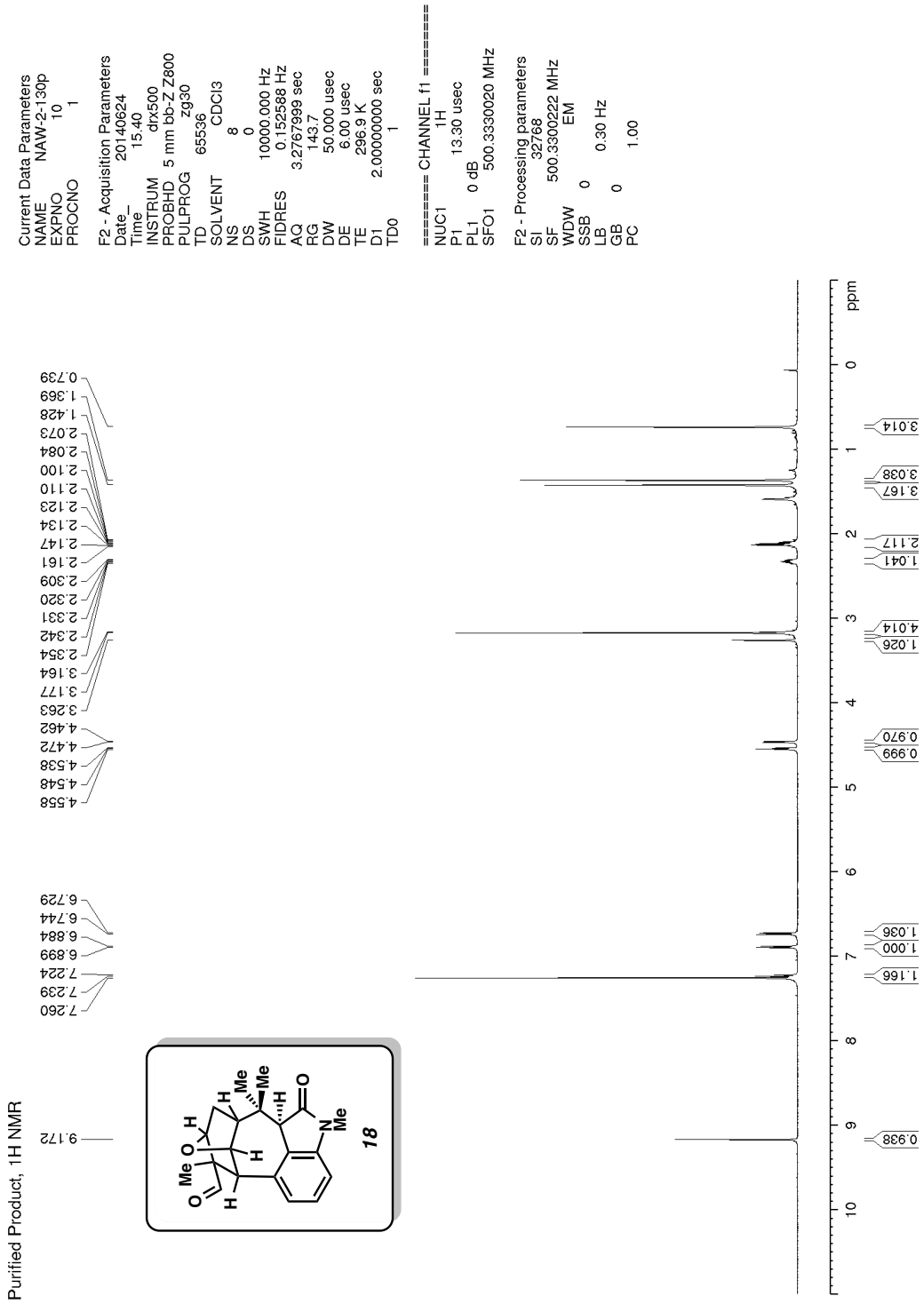
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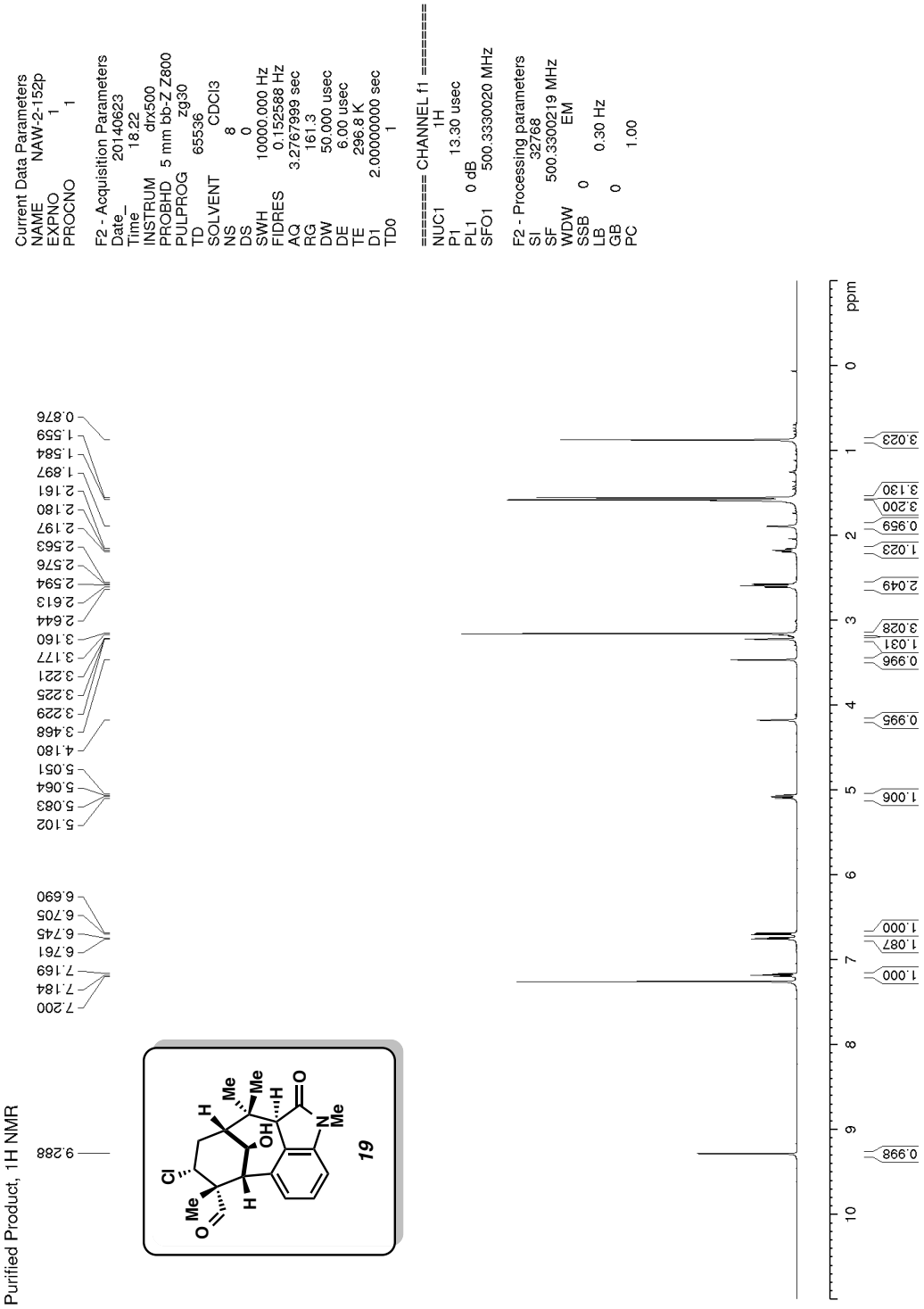
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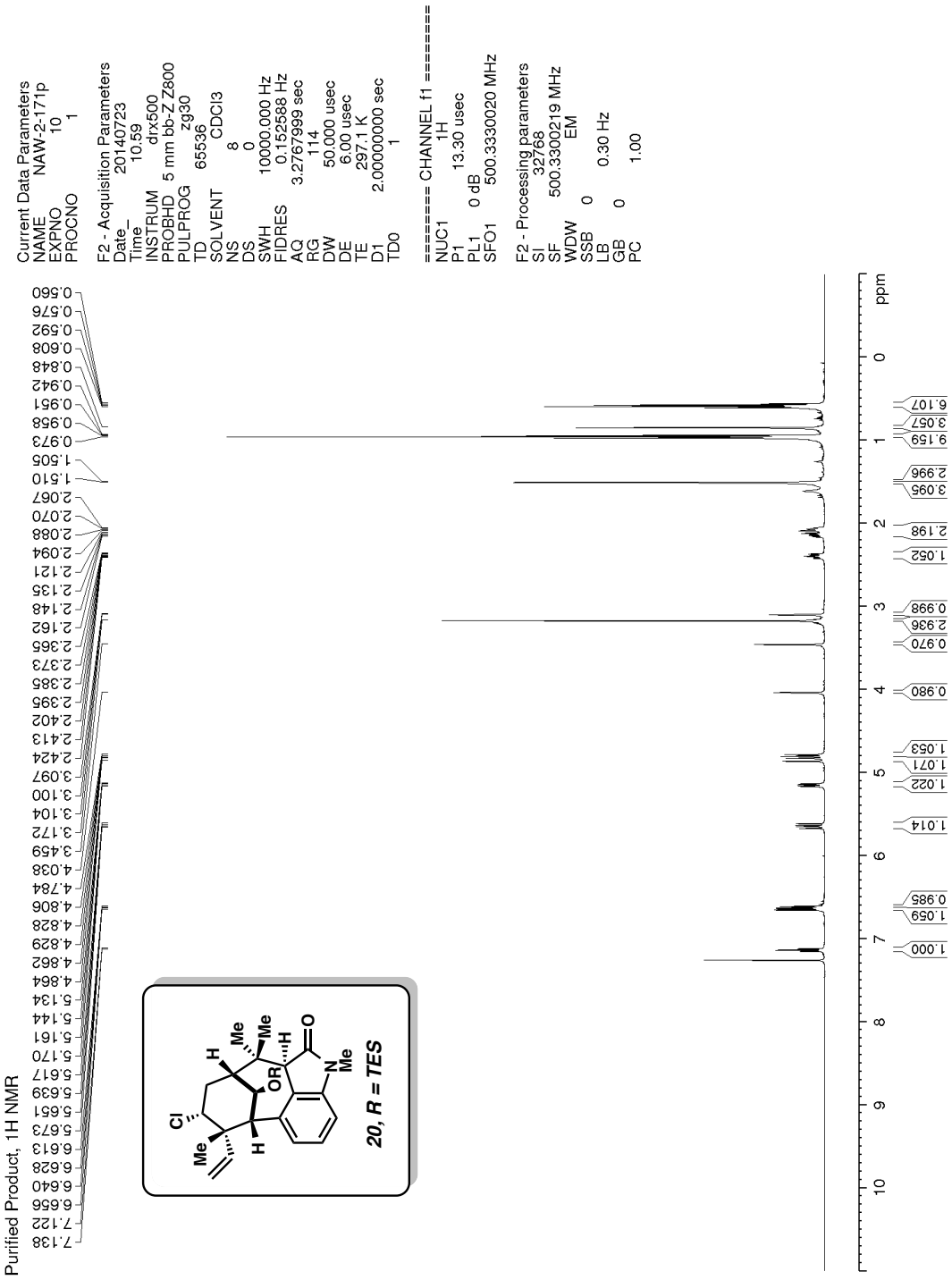
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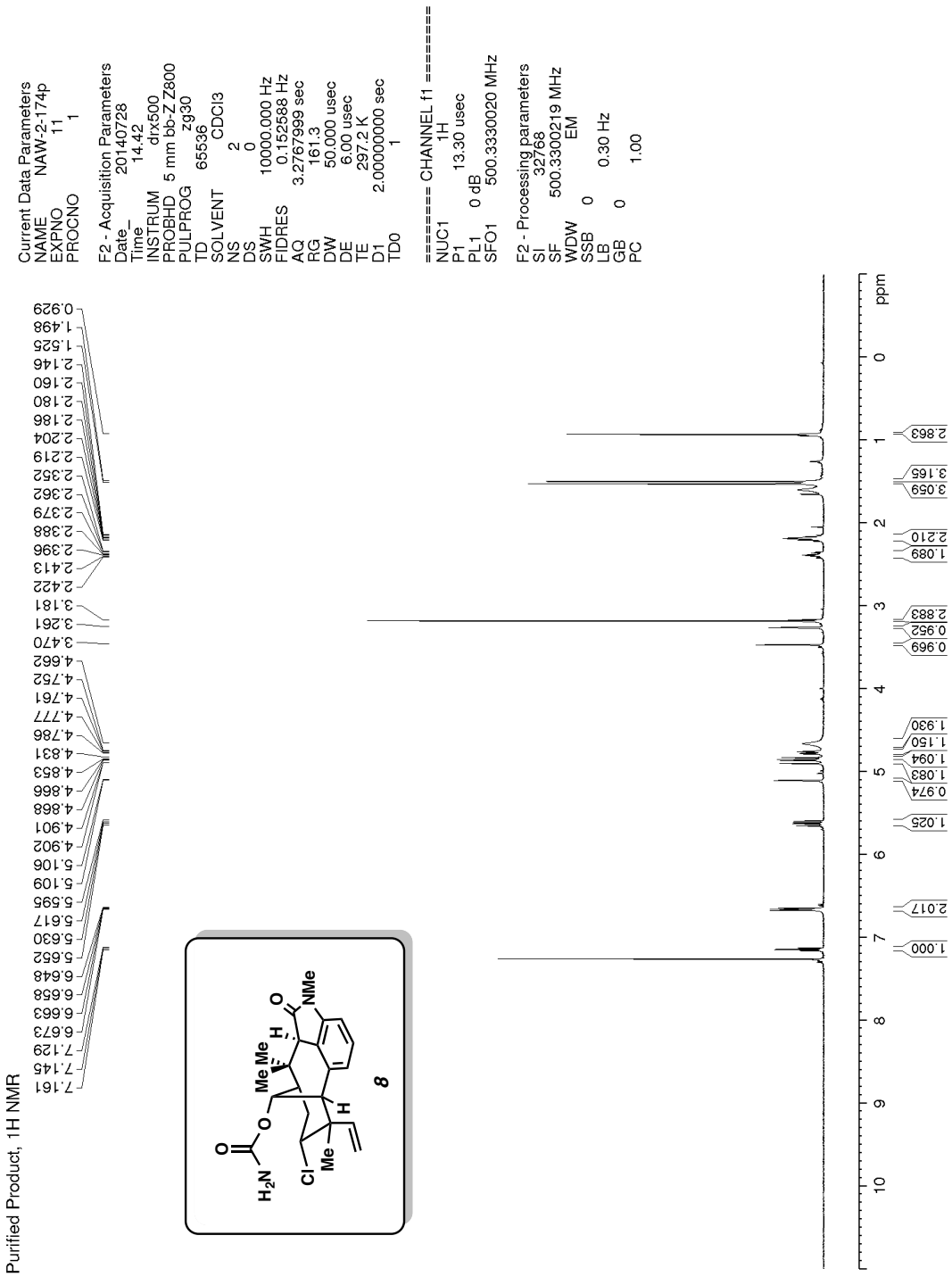
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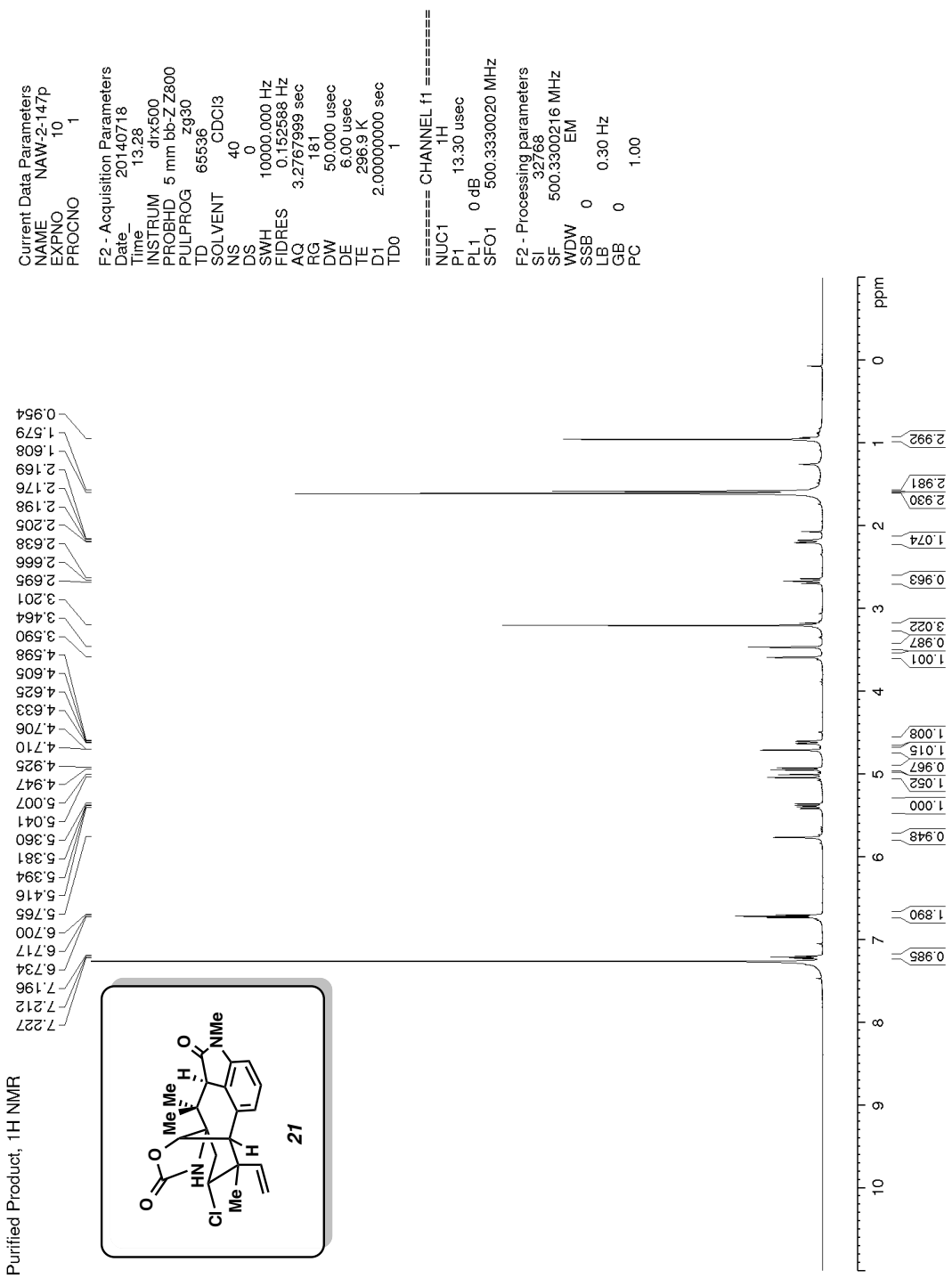
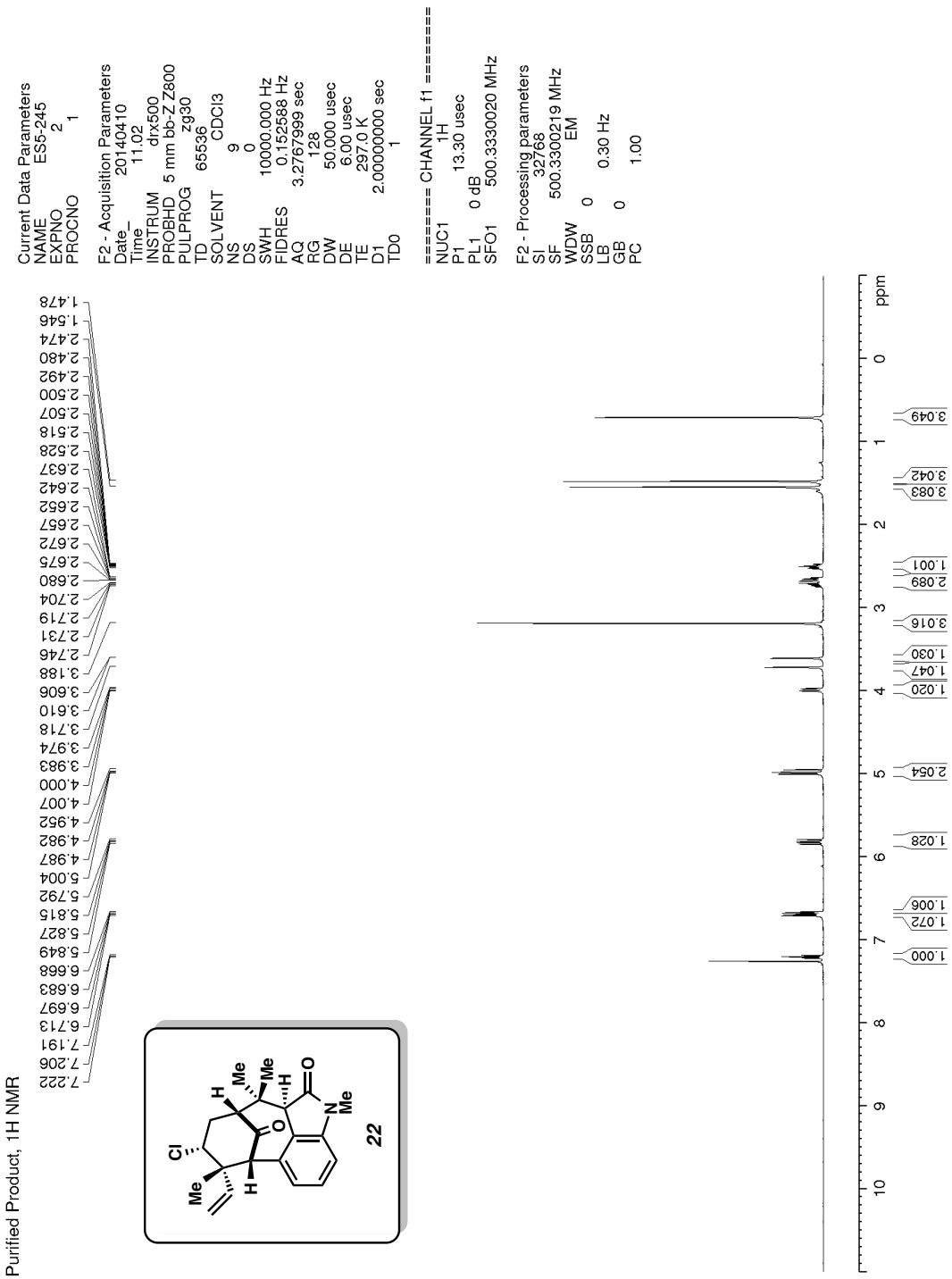
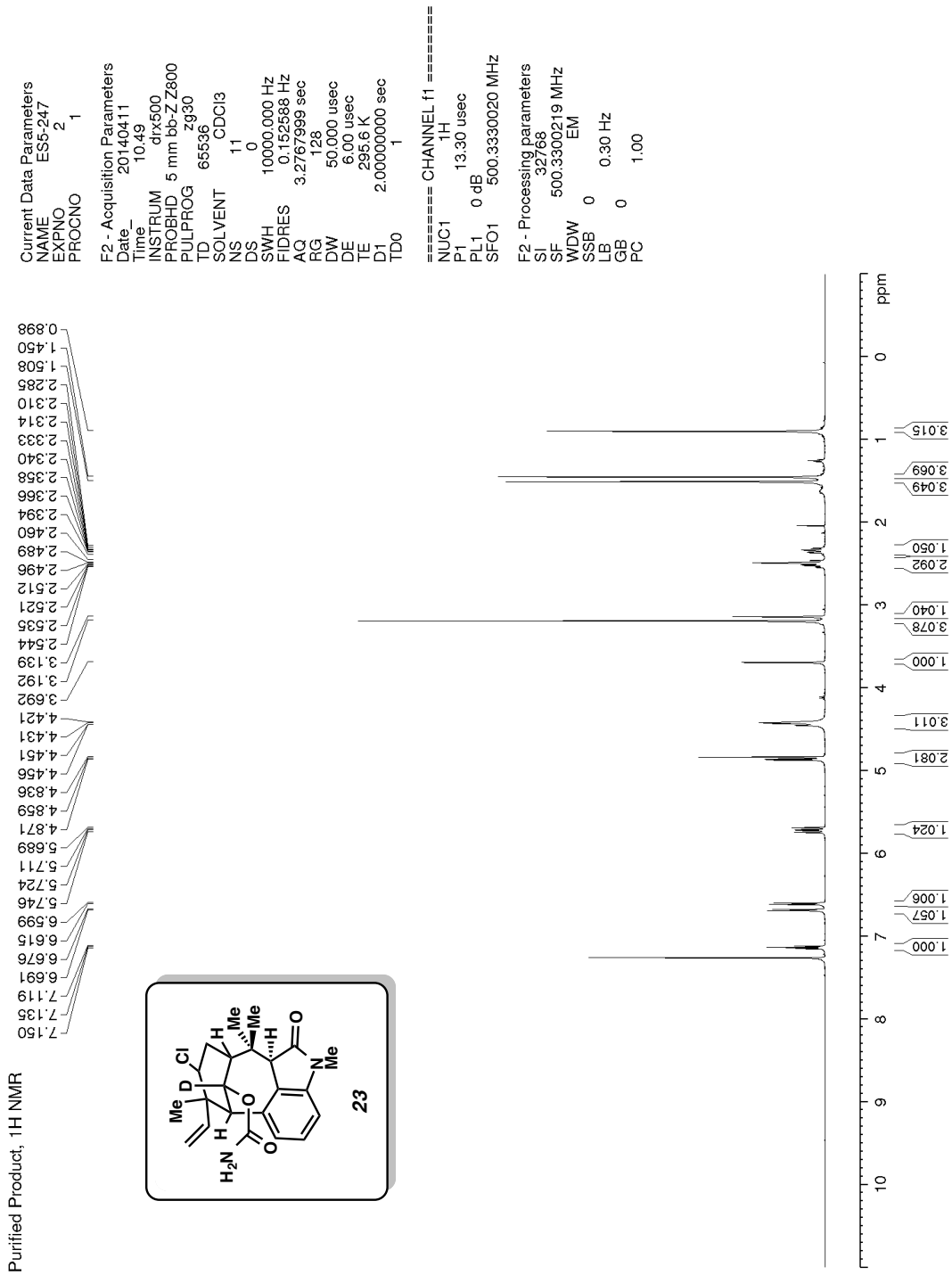
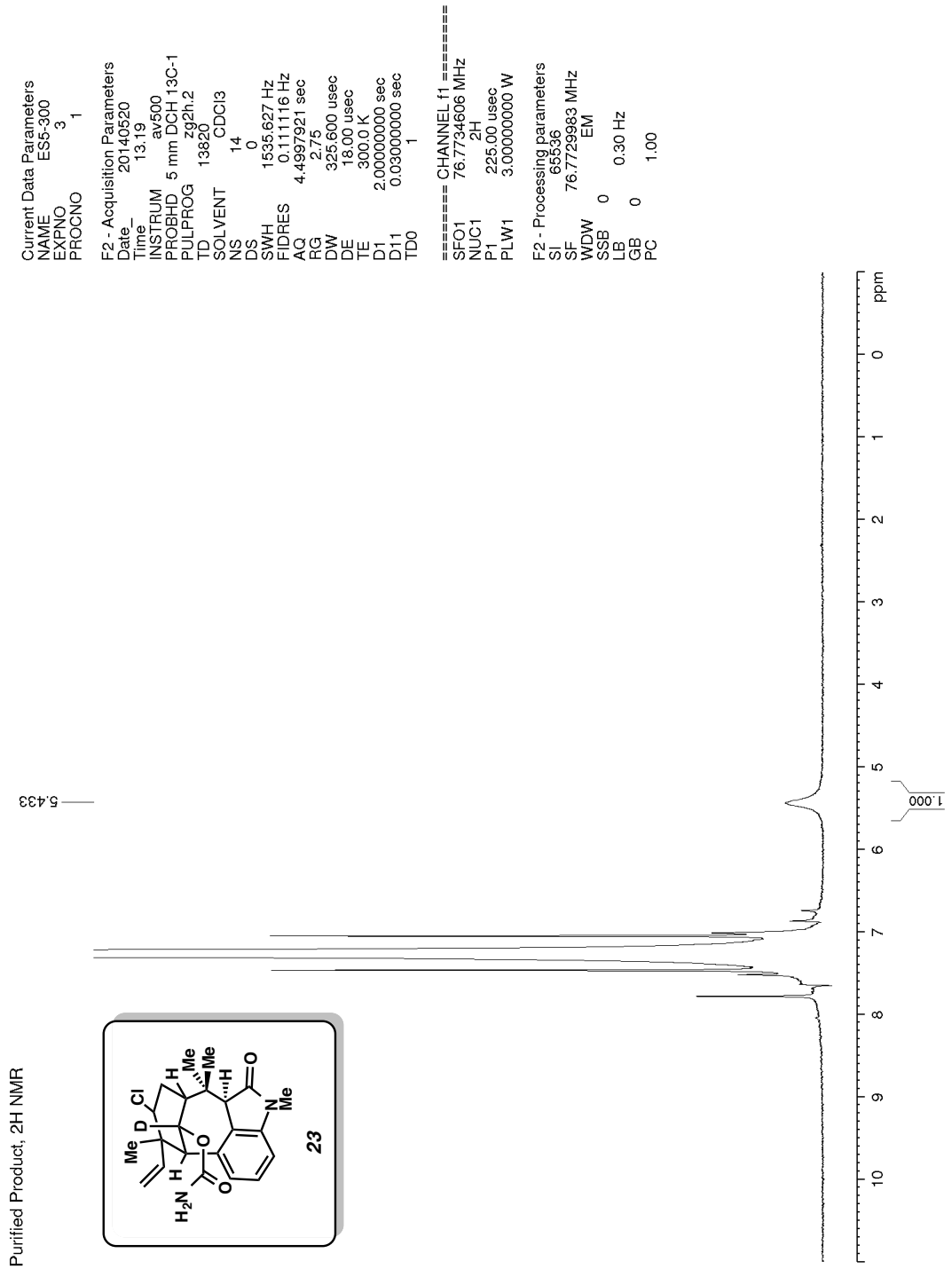
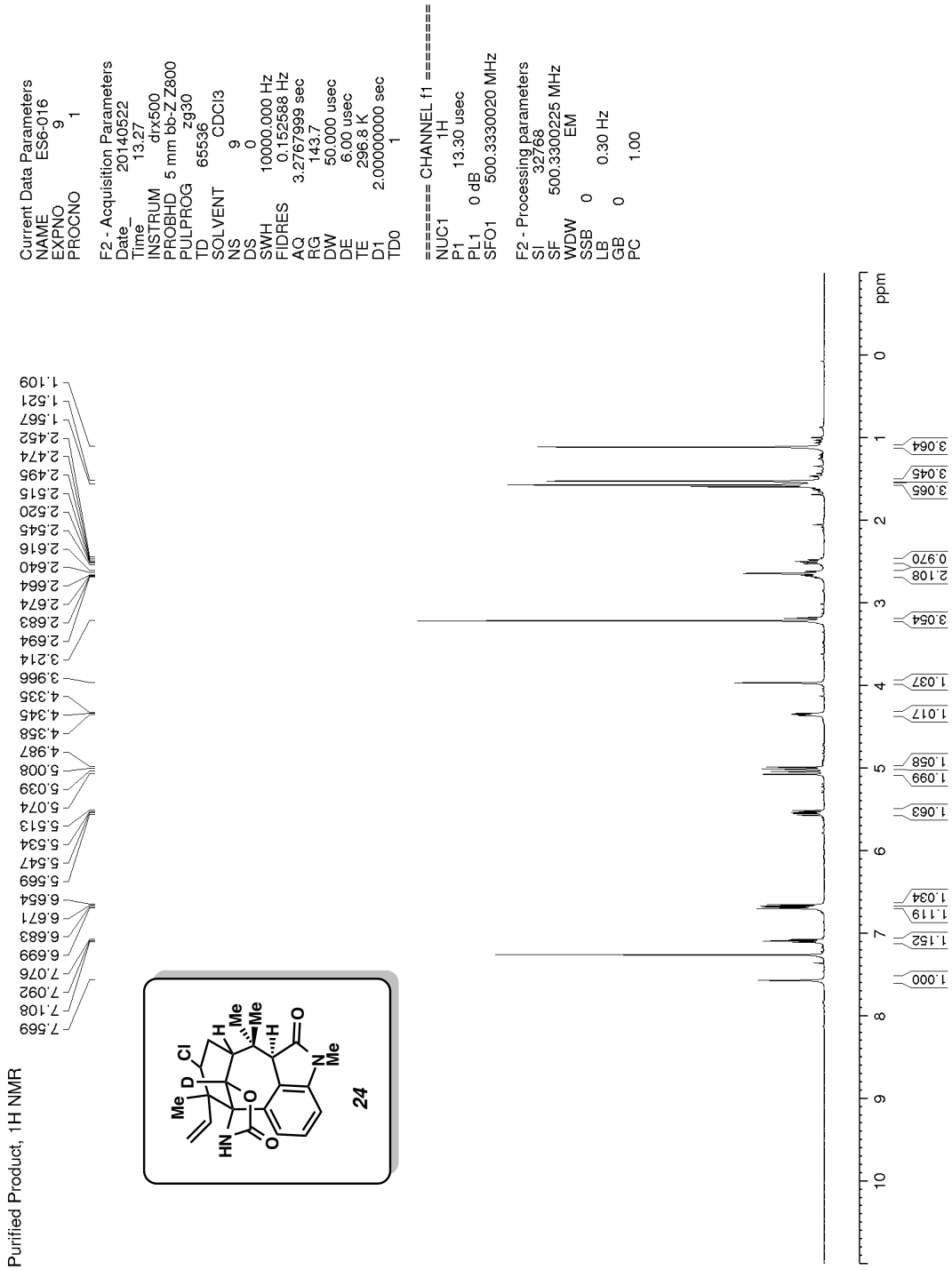
8
ppm

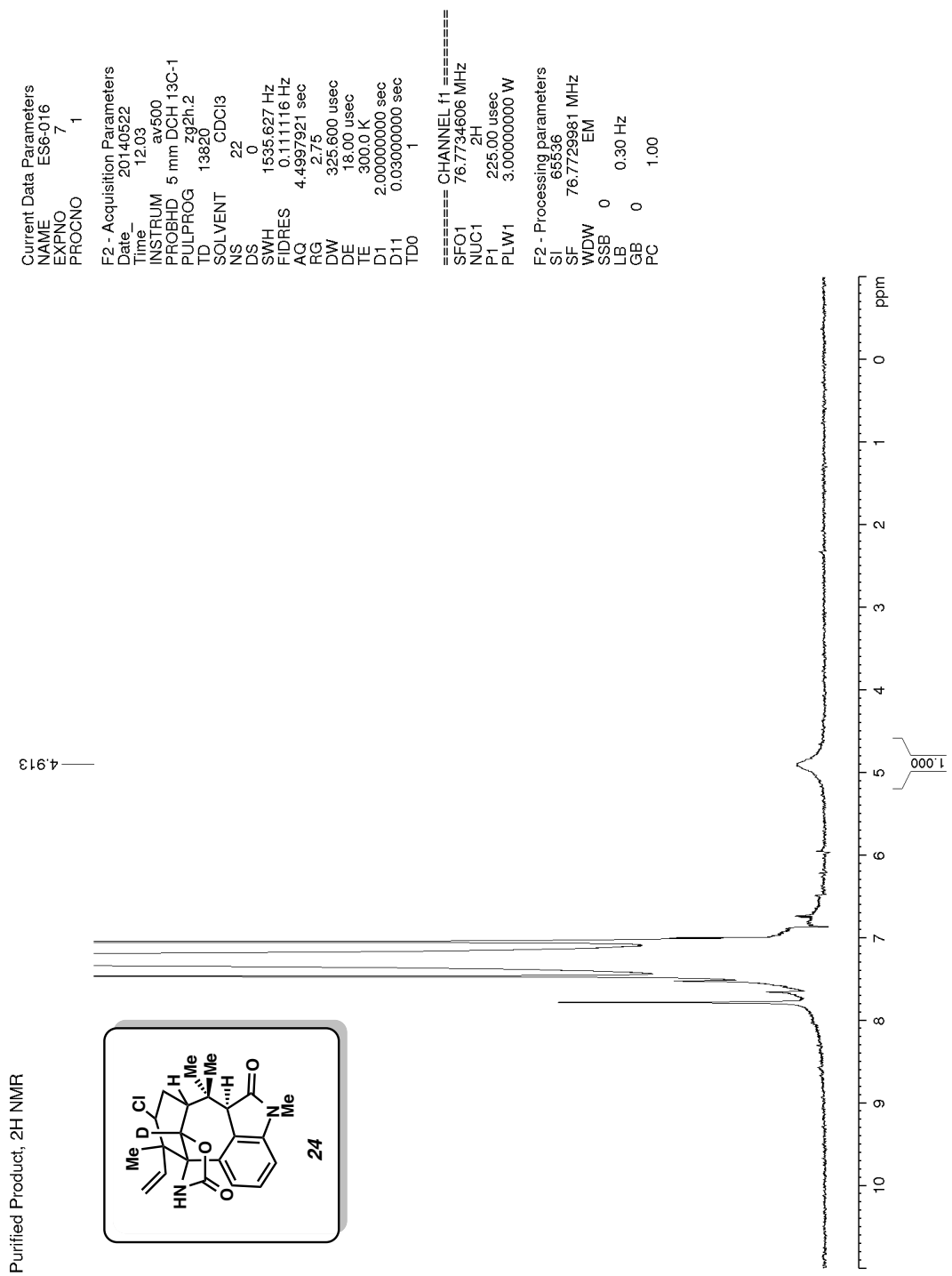

Purified Product, 1H NMR
21
Current Data Parameters
NAME NAW-2-147p
EXPNO 10
PROCNO 1
F2 - Acquisition Parameters
Date_ 20140718
Time_ 13.28
INSTRUM drx500
PROBHD 5 mm bb-Z Z800
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 40
DS 0
SWH 10000.000 Hz
FIDRES 0.152588 Hz
AQ 3.2767999 sec
RG 181
DW 50.000 usec
DE 6.00 usec
TE 296.9 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.30 usec
PL1 0 dB
SFO1 500.3330020 MHz
F2 - Processing parameters
SI 32768
SF 500.3300216 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
ppm

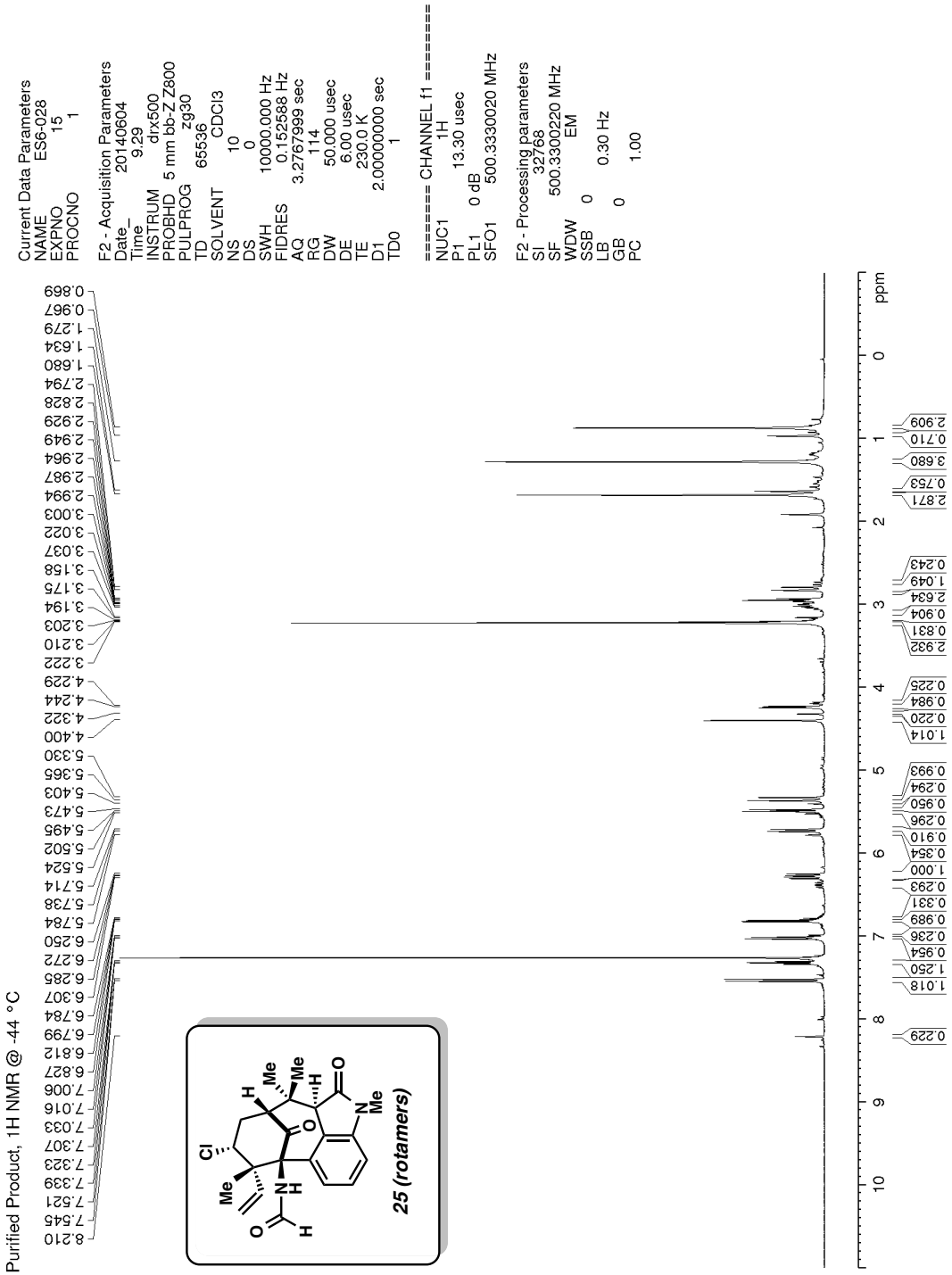

Purified Product, 1H NMR
Current Data Parameters
NAME ES5-245
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20140410
Time 11.02
INSTRUM drx500
PROBHD 5 mm bb-Z Z800
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 9
DS 0
SWH 10000.000 Hz
FIDRES 0.152588 Hz
AQ 3.2767999 sec
RG 128
DW 50.000 usec
DE 6.00 usec
TE 297.0 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.30 usec
PL1 0 dB
SFO1 500.3330020 MHz
F2 - Processing parameters
SI 32768
SF 500.3300219 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1.478
1.546
2.474
2.480
2.492
2.500
2.507
2.518
2.528
2.637
2.642
2.652
2.657
2.672
2.675
2.680
2.704
2.719
2.731
2.746
3.188
3.606
3.610
3.718
3.974
3.983
4.000
4.007
4.952
4.982
4.987
5.004
5.792
5.815
5.827
5.849
6.668
6.683
6.697
6.713
7.191
7.206
7.222
Me
Me
H
O
O
N
Me
Cl
Me
H
22
3.049
3.042
3.083
2.089
1.001
3.016
1.030
1.047
1.020
2.054
1.028
1.072
1.006
1.000
ppm

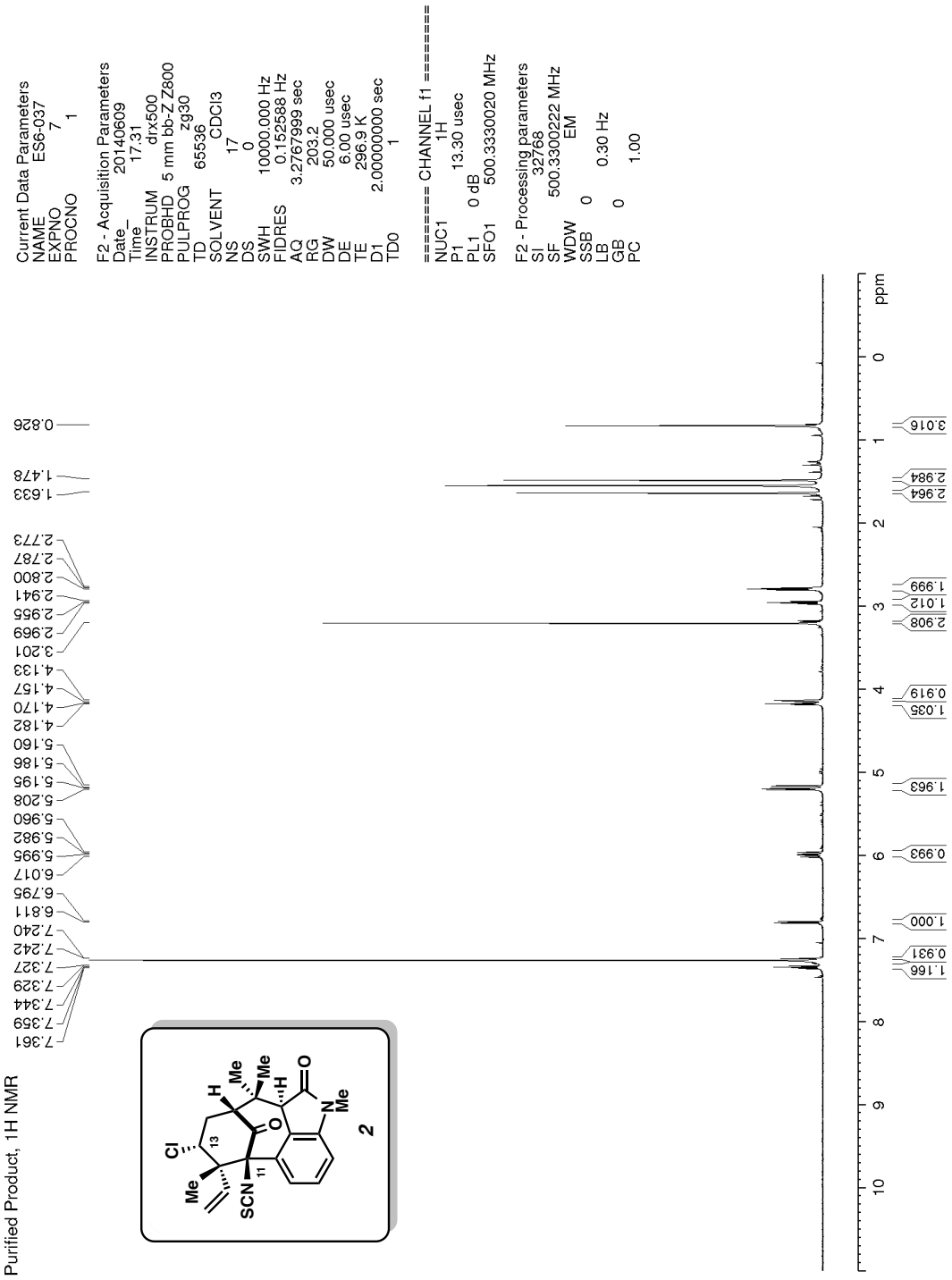

Purified Product, 1H NMR
Current Data Parameters
NAME ES5-247
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20140411
Time_ 10.49
INSTRUM drx500
PROBHD 5 mm bb-Z Z800
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 11
DS 0
SWH 10000.000 Hz
FIDRES 0.152588 Hz
AQ 3.2767999 sec
RG 128
DW 50.000 usec
DE 6.00 usec
TE 295.6 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.30 usec
PL1 0 dB
SFO1 500.3330020 MHz
F2 - Processing parameters
SI 32768
SF 500.3300219 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
0.898
1.450
1.508
2.285
2.310
2.314
2.333
2.340
2.358
2.366
2.394
2.460
2.489
2.496
2.512
2.521
2.535
2.544
3.139
3.192
3.692
4.421
4.431
4.451
4.456
4.836
4.859
4.871
5.689
5.711
5.724
5.746
6.599
6.615
6.676
6.691
7.119
7.135
7.150
3.015
3.069
3.049
2.092
1.050
1.040
3.078
1.000
3.011
2.081
1.024
1.057
1.006
1.000
ppm
23


Purified Product, 2H NMR
23
5.433
1.000
ppm
Current Data Parameters
NAME ES5-300
EXPNO 3
PROCNO 1
F2 - Acquisition Parameters
Date_ 20140520
Time_ 13.19
INSTRUM av500
PROBHD 5 mm DCH 13C-1
PULPROG zg2h.2
TD 13820
SOLVENT CDCl3
NS 14
DS 0
SWH 1535.627 Hz
FIDRES 0.111116 Hz
AQ 4.4997921 sec
RG 2.75
DW 325.600 usec
DE 18.00 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 76.7734606 MHz
NUC1 2H
P1 225.00 usec
PLW1 3.00000000 W
F2 - Processing parameters
SI 65536
SF 76.7729983 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

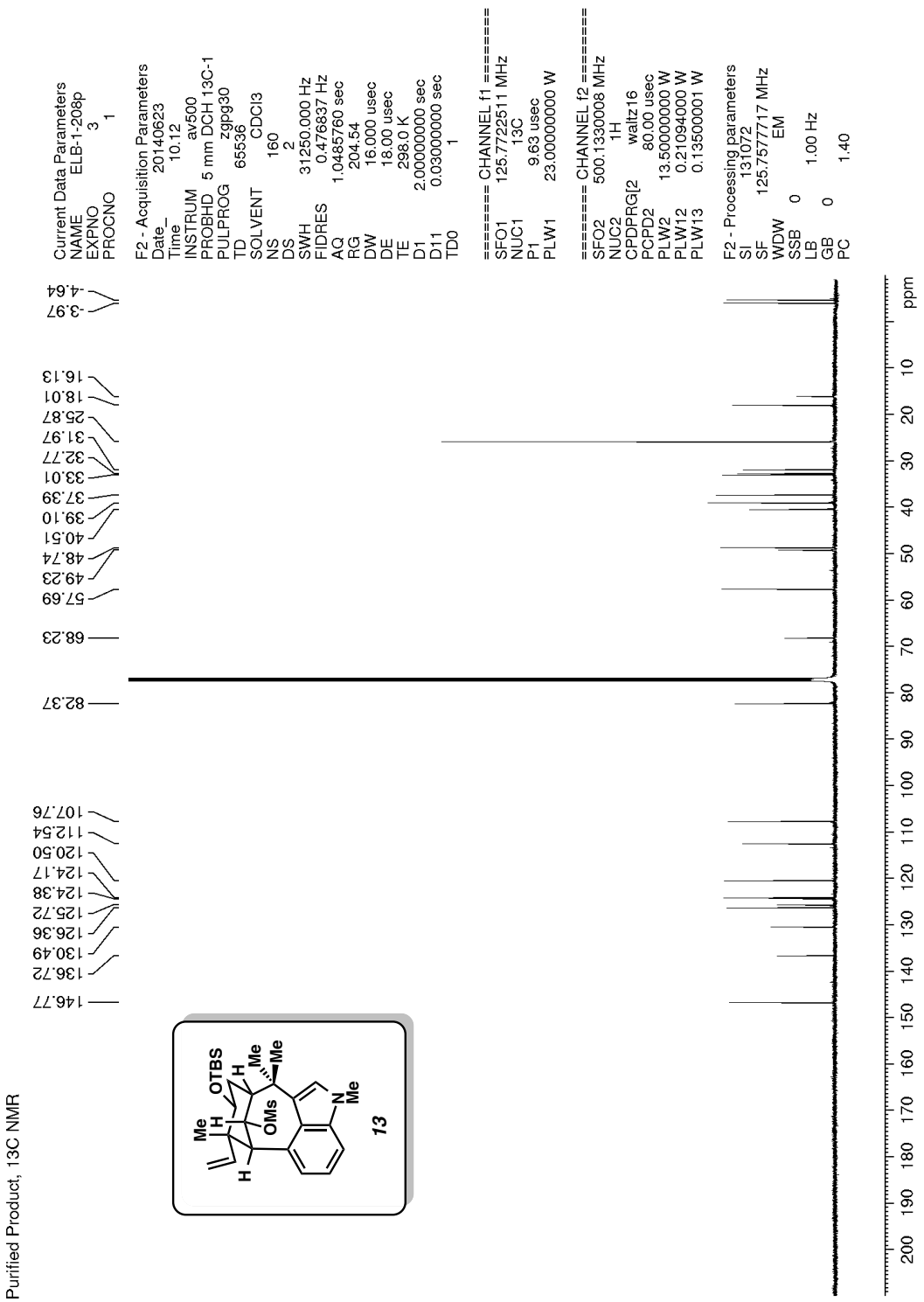

Purified Product, 1H NMR
Current Data Parameters
NAME ES6-016
EXPNO 9
PROCNO 1
F2 - Acquisition Parameters
Date_ 20140522
Time 13.27
INSTRUM drx500
PROBHD 5 mm bb-Z Z800
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 9
DS 0
SWH 10000.000 Hz
FIDRES 0.152588 Hz
AQ 3.2767999 sec
RG 143.7
DW 50.000 usec
DE 6.00 usec
TE 296.8 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.30 usec
PL1 0 dB
SFO1 500.3330020 MHz
F2 - Processing parameters
SI 32768
SF 500.3300225 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
7.569
7.108
7.092
7.076
6.699
6.683
6.671
6.654
5.569
5.547
5.534
5.513
5.074
5.039
5.008
4.987
4.358
4.345
4.335
3.966
3.214
2.694
2.683
2.674
2.664
2.640
2.616
2.545
2.520
2.515
2.495
2.474
2.452
1.567
1.521
1.109
Me
D
Cl
H
Me
Me
H
O
N
Me
HN
O
O
24
1.000
1.152
1.119
1.034
1.063
1.099
1.058
1.037
1.017
3.054
2.108
0.970
3.065
3.045
3.064
ppm

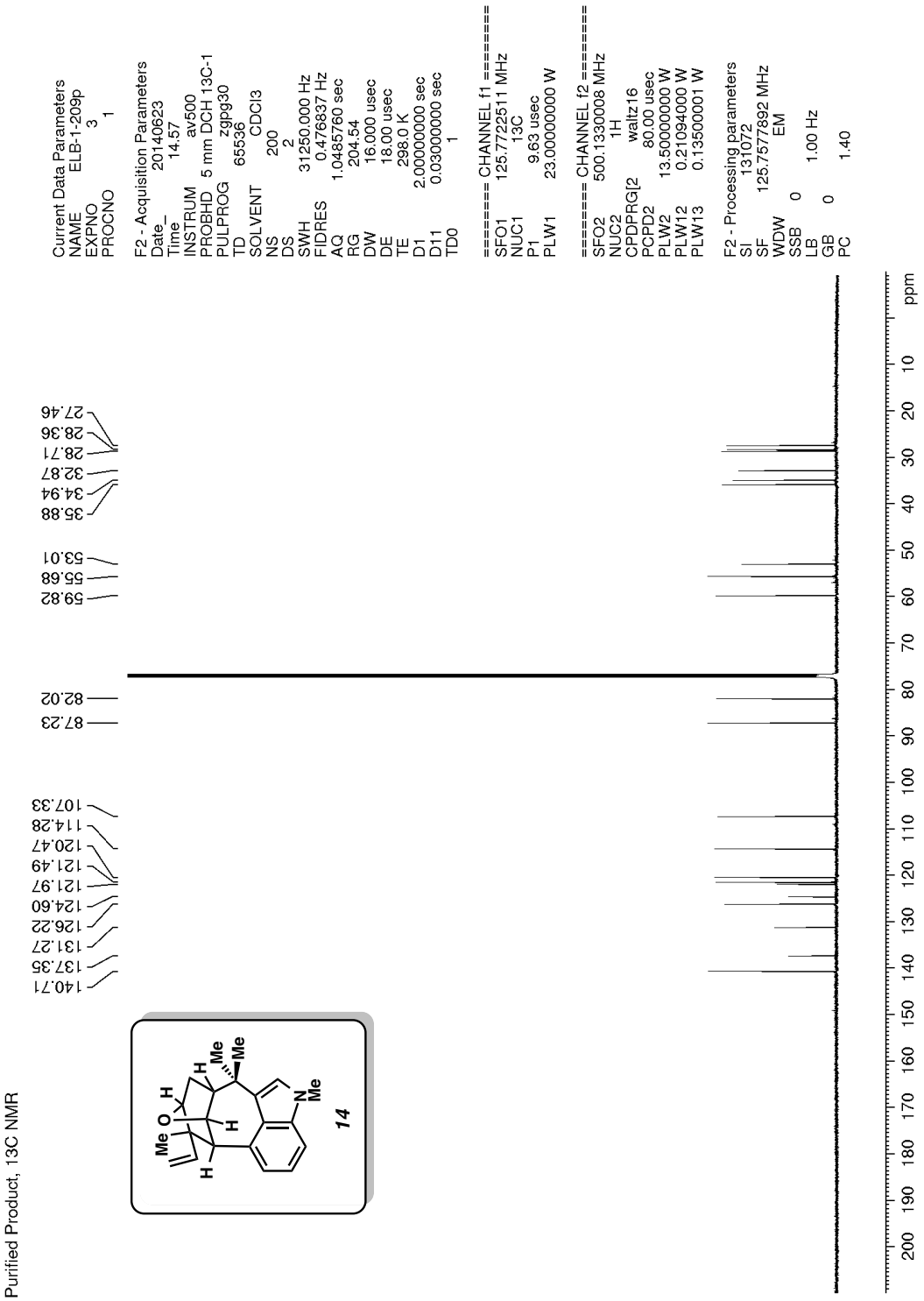

Purified Product, 2H NMR
4.913
24
Current Data Parameters
NAME ES6-016
EXPNO 7
PROCNO 1
F2 - Acquisition Parameters
Date_ 20140522
Time_ 12.03
INSTRUM av500
PROBHD 5 mm DCH 13C-1
PULPROG zg2h.2
TD 13820
SOLVENT CDCl3
NS 22
DS 0
SWH 1535.627 Hz
FIDRES 0.111116 Hz
AQ 4.4997921 sec
RG 2.75
DW 325.600 usec
DE 18.00 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 76.7734606 MHz
NUC1 2H
P1 225.00 usec
PLW1 3.00000000 W
F2 - Processing parameters
SI 65536
SF 76.7729981 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1.000
ppm

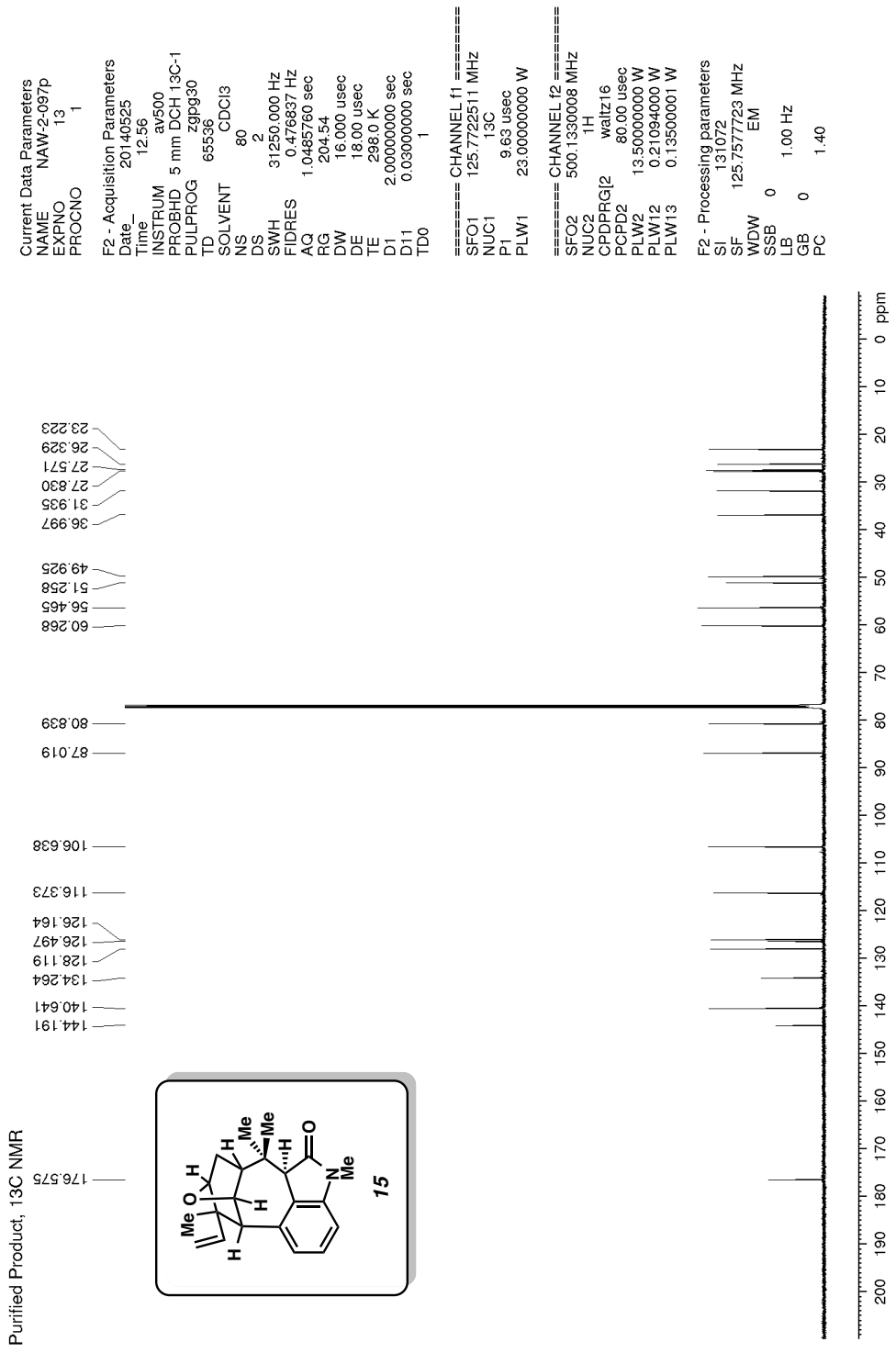

Purified Product, 1H NMR @ -44 °C
Current Data Parameters
NAME ES6-028
EXPNO 15
PROCNO 1
F2 - Acquisition Parameters
Date_ 20140604
Time_ 9.29
INSTRUM drx500
PROBHD 5 mm bb-Z Z800
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 10
DS 0
SWH 10000.000 Hz
FIDRES 0.152588 Hz
AQ 3.2767999 sec
RG 114
DW 50.000 usec
DE 6.00 usec
TE 230.0 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.30 usec
PL1 0 dB
SFO1 500.3330020 MHz
F2 - Processing parameters
SI 32768
SF 500.3300220 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
25 (rotamers)
ppm

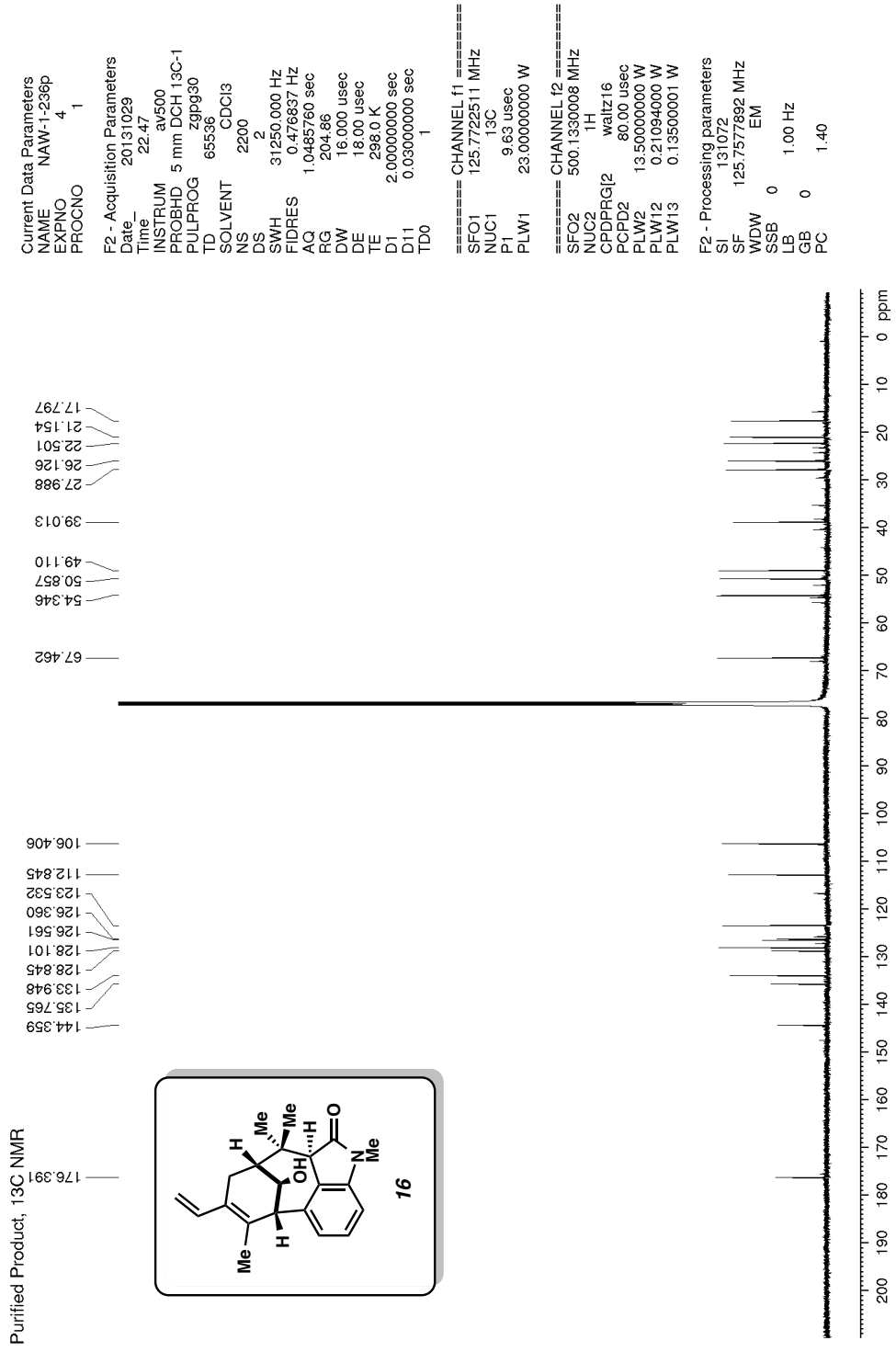

Purified Product, 1H NMR
Current Data Parameters
NAME ES6-037
EXPNO 7
PROCNO 1
F2 - Acquisition Parameters
Date_ 20140609
Time 17.31
INSTRUM drx500
PROBHD 5 mm bb-Z Z800
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 17
DS 0
SWH 10000.000 Hz
FIDRES 0.152588 Hz
AQ 3.2767999 sec
RG 203.2
DW 50.000 usec
DE 6.00 usec
TE 296.9 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.30 usec
PL1 0 dB
SFO1 500.3330020 MHz
F2 - Processing parameters
SI 32768
SF 500.3300222 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
0.826
1.478
1.633
2.773
2.787
2.800
2.941
2.955
2.969
3.201
4.133
4.157
4.170
4.182
5.160
5.186
5.195
5.208
5.960
5.982
5.995
6.017
6.795
6.811
7.240
7.242
7.327
7.329
7.344
7.359
7.361
3.016
2.964
2.984
2.908
1.012
1.999
1.035
0.919
1.963
0.993
1.000
0.931
1.166
ppm
Me
H
Me
Me
H
O
O
N
Me
Cl
13
11
SCN
Me
2

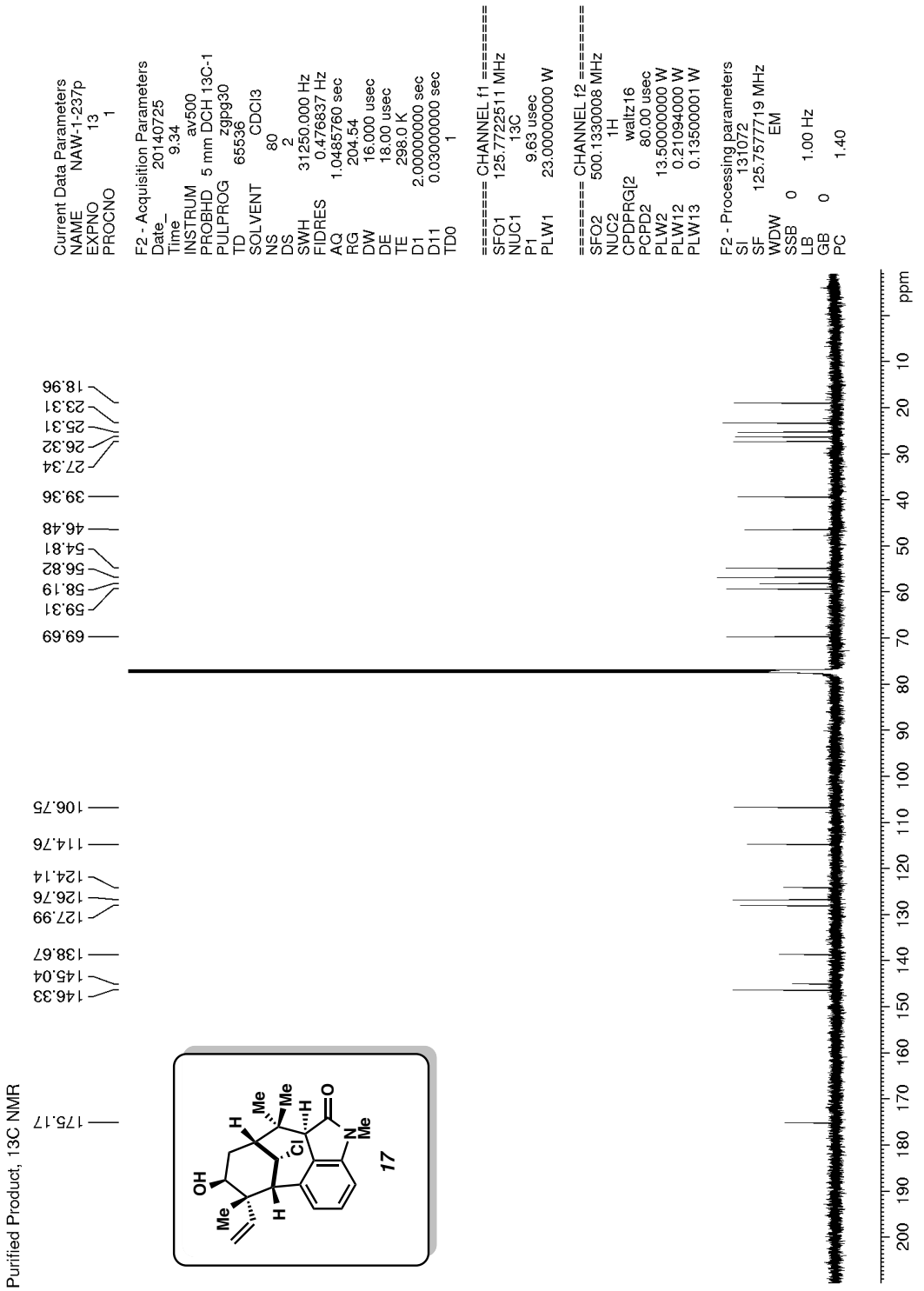
^{13}C NMR Spectra:

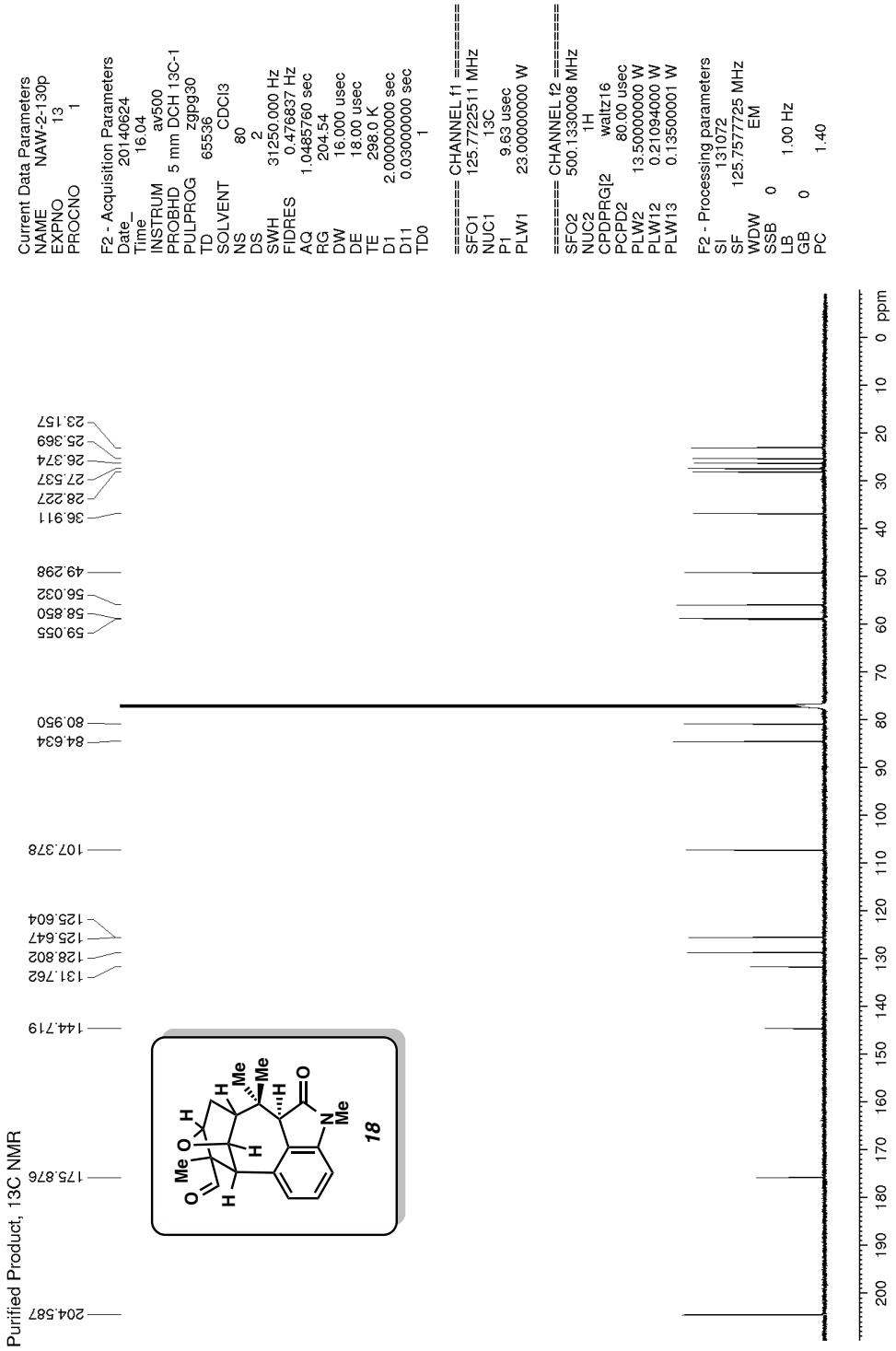

Purified Product, 13C NMR
Current Data Parameters
NAME ELB-1-208p
EXPNO 3
PROCNO 1
F2 - Acquisition Parameters
Date_ 20140623
Time_ 10.12
INSTRUM av500
PROBHD 5 mm DCH 13C-1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 160
DS 2
SWH 31250.000 Hz
FIDRES 0.476837 Hz
AQ 1.0485760 sec
RG 204.54
DW 16.000 usec
DE 18.00 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 125.7722511 MHz
NUC1 13C
P1 9.63 usec
PLW1 23.00000000 W
======== CHANNEL f2 ========
SFO2 500.1330008 MHz
NUC2 1H
CPDPRG[2 waltz16
POPD2 80.00 usec
PLW2 13.50000000 W
PLW12 0.21094000 W
PLW13 0.13500001 W
F2 - Processing parameters
SI 131072
SF 125.7577717 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
-4.64
-3.97
16.13
18.01
25.87
31.97
32.77
33.01
37.39
39.10
40.51
48.74
49.23
57.69
68.23
82.37
107.76
112.54
120.50
124.17
124.38
125.72
126.36
130.49
136.72
146.77
Me
H
H
OTBS
H
Me
Me
OMs
N
Me
13
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

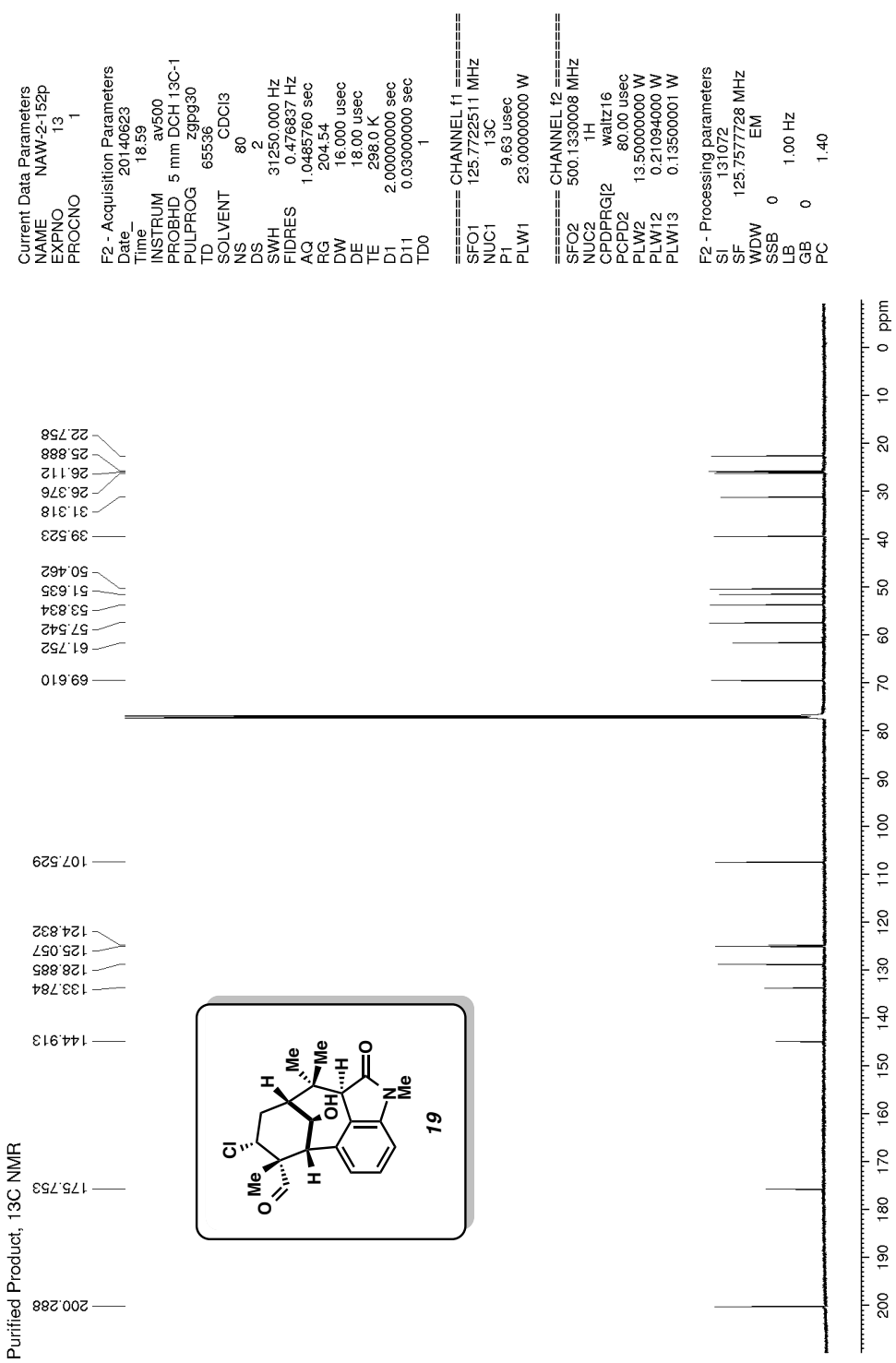

Purified Product, 13C NMR
140.71
137.35
131.27
126.22
124.60
121.97
121.49
120.47
114.28
107.33
87.23
82.02
59.82
55.68
53.01
35.88
34.94
32.87
28.71
28.36
27.46
Me
O
H
H
H
Me
Me
N
Me
14
Current Data Parameters
NAME ELB-1-209p
EXPNO 3
PROCNO 1
F2 - Acquisition Parameters
Date_ 20140623
Time 14.57
INSTRUM av500
PROBHD 5 mm DCH 13C-1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 200
DS 2
SWH 31250.000 Hz
FIDRES 0.476837 Hz
AQ 1.0485760 sec
RG 204.54
DW 16.000 usec
DE 18.00 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 125.7722511 MHz
NUC1 13C
P1 9.63 usec
PLW1 23.00000000 W
======== CHANNEL f2 ========
SFO2 500.1330008 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 13.50000000 W
PLW12 0.21094000 W
PLW13 0.13500001 W
F2 - Processing parameters
SI 131072
SF 125.7577892 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

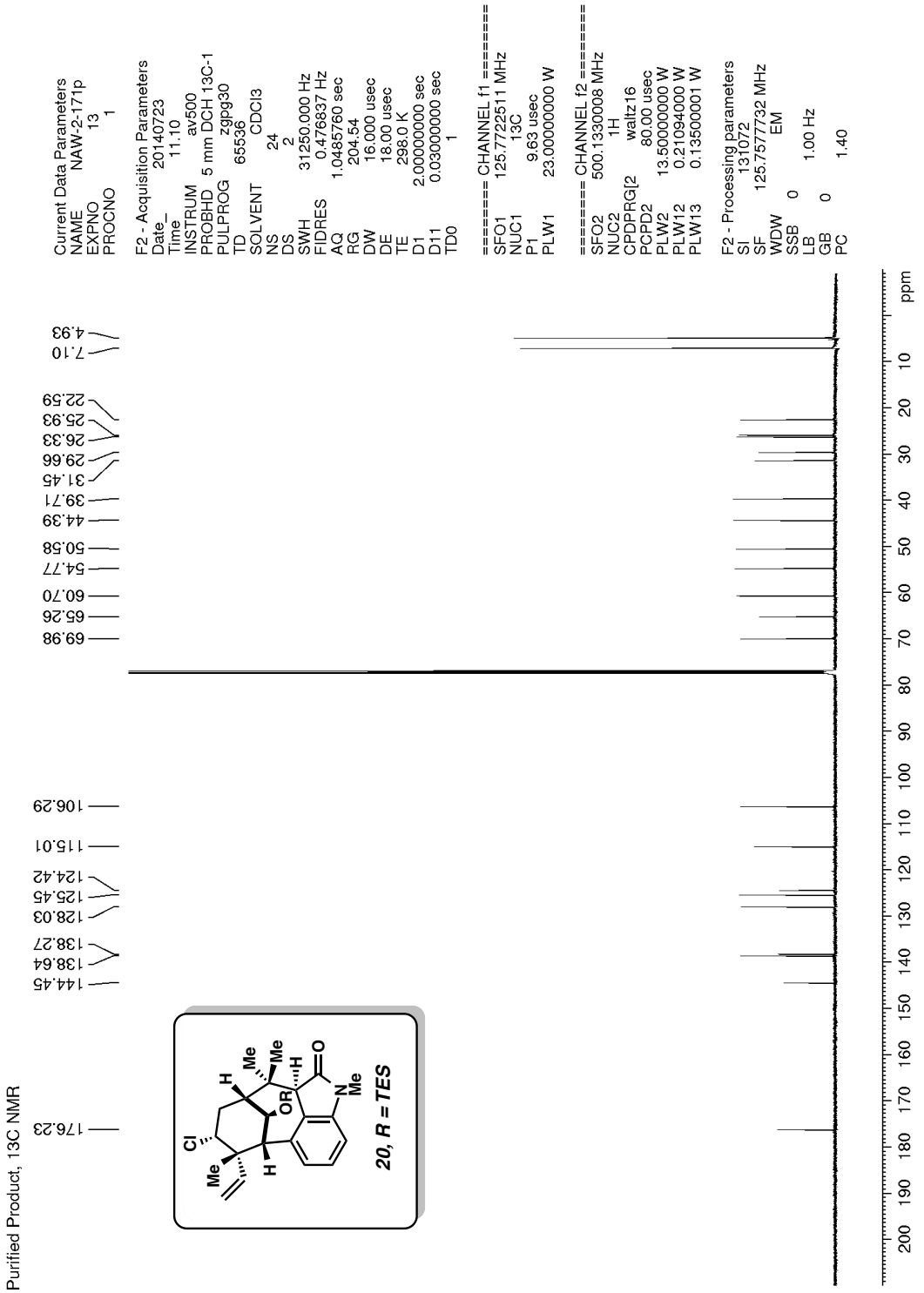

Purified Product, 13C NMR
Current Data Parameters
NAME NAW-2-097p
EXPNO 13
PROCNO 1
F2 - Acquisition Parameters
Date_ 20140525
Time 12.56
INSTRUM av500
PROBHD 5 mm DCH 13C-1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 80
DS 2
SWH 31250.000 Hz
FIDRES 0.476837 Hz
AQ 1.0485760 sec
RG 204.54
DW 16.000 usec
DE 18.00 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 125.7722511 MHz
NUC1 13C
P1 9.63 usec
PLW1 23.00000000 W
======== CHANNEL f2 ========
SFO2 500.1330008 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 13.50000000 W
PLW12 0.21094000 W
PLW13 0.13500001 W
F2 - Processing parameters
SI 131072
SF 125.7577723 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
176.575
144.191
140.641
134.264
128.119
126.497
126.164
116.373
106.638
87.019
80.839
60.268
56.465
51.258
49.925
36.997
31.935
27.830
27.571
26.329
23.223
15
ppm

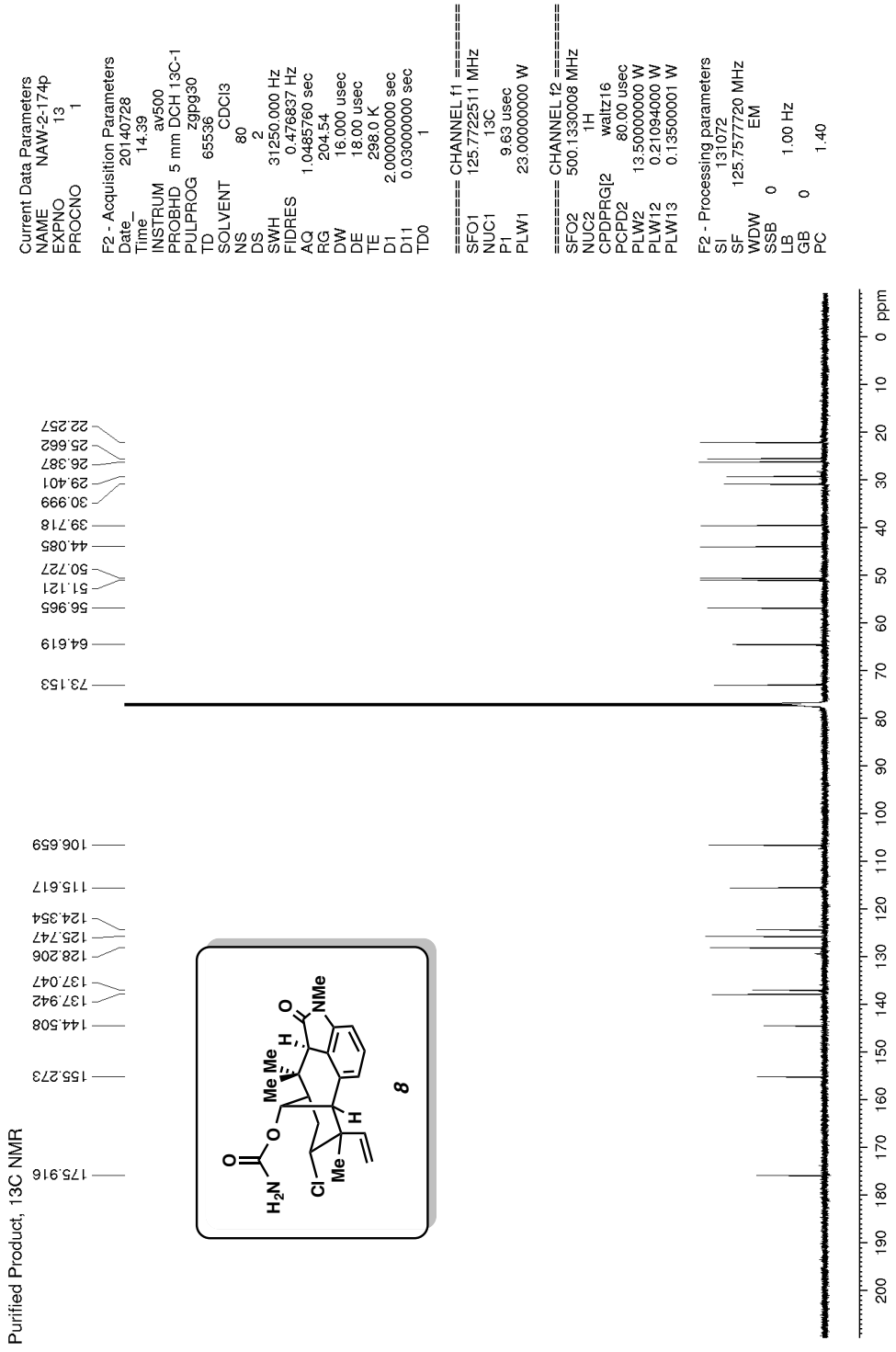

Purified Product, 13C NMR
176.391
144.359
135.765
133.948
128.845
128.101
126.561
126.360
123.532
112.845
106.406
67.462
54.346
50.857
49.110
39.013
27.988
26.126
22.501
21.154
17.797
16
Current Data Parameters
NAME NAW-1-236p
EXPNO 4
PROCNO 1
F2 - Acquisition Parameters
Date_ 20131029
Time 22.47
INSTRUM av500
PROBHD 5 mm DCH 13C-1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2200
DS 2
SWH 31250.000 Hz
FIDRES 0.476837 Hz
AQ 1.0485760 sec
RG 204.86
DW 16.000 usec
DE 18.00 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 125.7722511 MHz
NUC1 13C
P1 9.63 usec
PLW1 23.00000000 W
======== CHANNEL f2 ========
SFO2 500.1330008 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 13.50000000 W
PLW12 0.21094000 W
PLW13 0.13500001 W
F2 - Processing parameters
SI 131072
SF 125.7577892 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

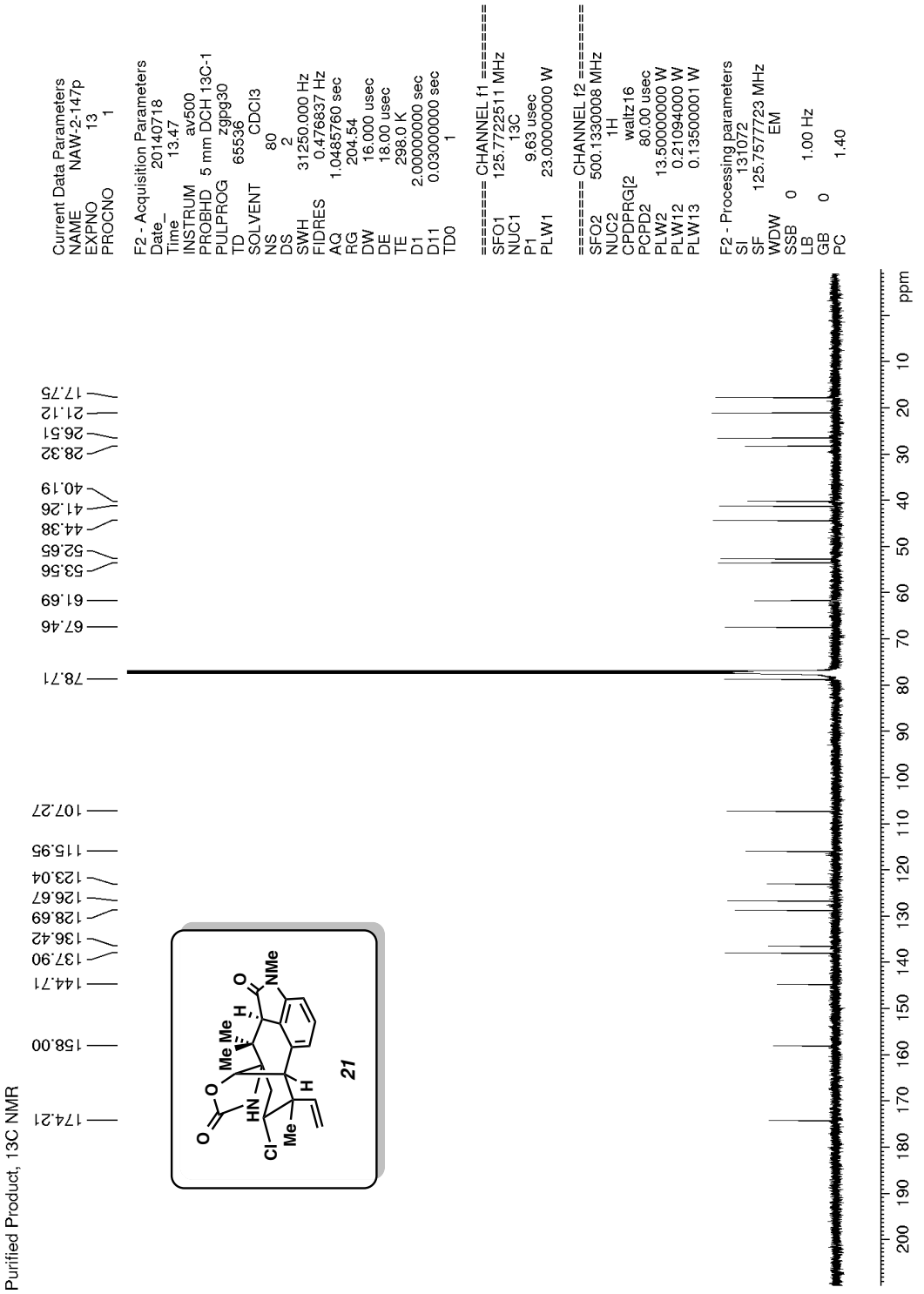

Purified Product, 13C NMR
Current Data Parameters
NAME NAW-1-237p
EXPNO 13
PROCNO 1
F2 - Acquisition Parameters
Date_ 20140725
Time_ 9.34
INSTRUM av500
PROBHD 5 mm DCH 13C-1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 80
DS 2
SWH 31250.000 Hz
FIDRES 0.476837 Hz
AQ 1.0485760 sec
RG 204.54
DW 16.000 usec
DE 18.00 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 125.7722511 MHz
NUC1 13C
P1 9.63 usec
PLW1 23.00000000 W
======== CHANNEL f2 ========
SFO2 500.1330008 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 13.50000000 W
PLW12 0.21094000 W
PLW13 0.13500001 W
F2 - Processing parameters
SI 131072
SF 125.7577719 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
175.17
146.33
145.04
138.67
127.99
126.76
124.14
114.76
106.75
69.69
59.31
58.19
56.82
54.81
46.48
39.36
27.34
26.32
25.31
23.31
18.96
17
ppm

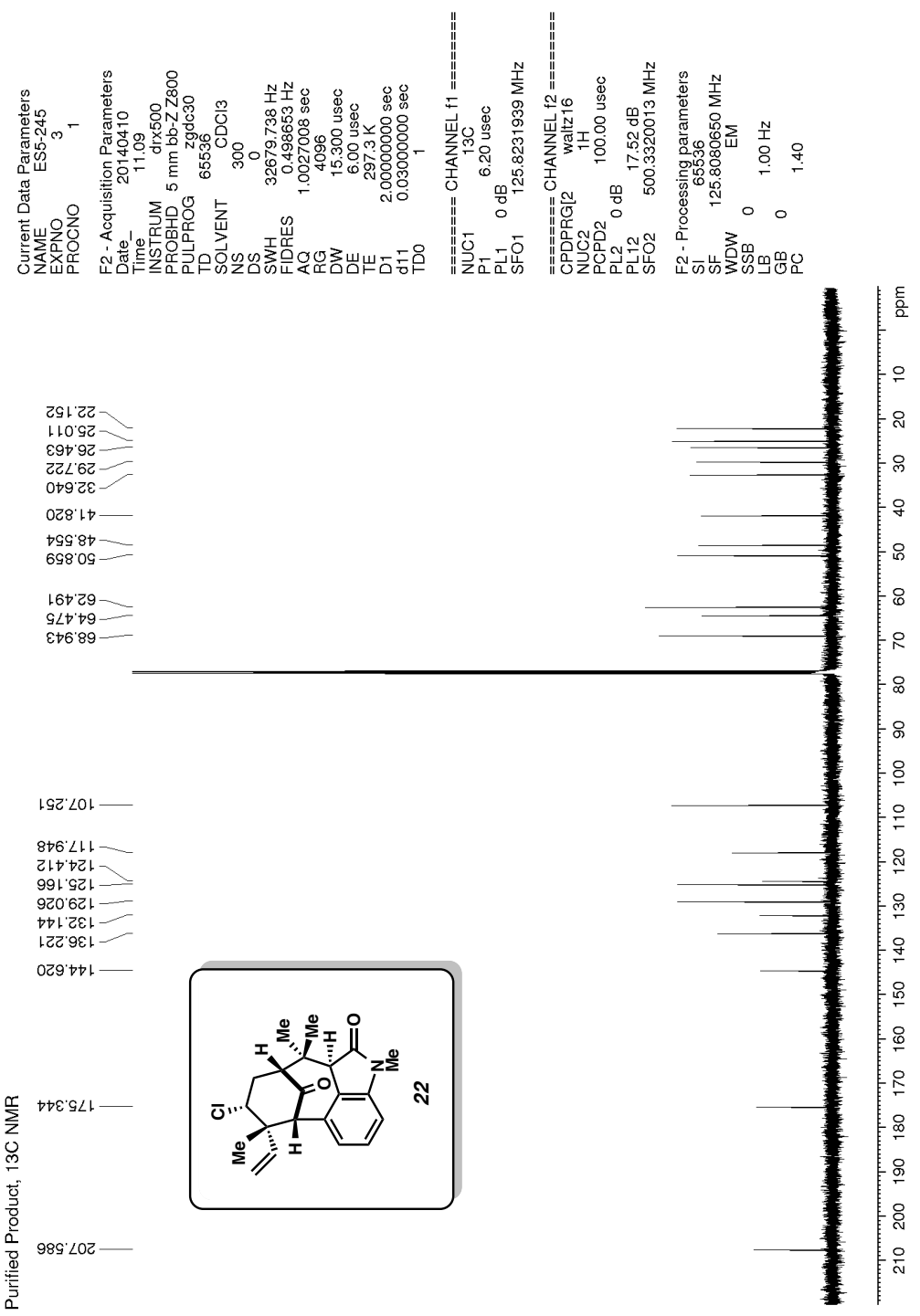

Purified Product, 13C NMR
Current Data Parameters
NAME NAW-2-130p
EXPNO 13
PROCNO 1
F2 - Acquisition Parameters
Date_ 20140624
Time 16.04
INSTRUM av500
PROBHD 5 mm DCH 13C-1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 80
DS 2
SWH 31250.000 Hz
FIDRES 0.476837 Hz
AQ 1.0485760 sec
RG 204.54
DW 16.000 usec
DE 18.00 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 125.7722511 MHz
NUC1 13C
P1 9.63 usec
PLW1 23.00000000 W
======== CHANNEL f2 ========
SFO2 500.1330008 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 13.50000000 W
PLW12 0.21094000 W
PLW13 0.13500001 W
F2 - Processing parameters
SI 131072
SF 125.7577725 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
204.587
175.876
144.719
131.762
128.802
125.647
125.604
107.378
84.634
80.950
59.055
58.850
56.032
49.298
36.911
28.227
27.537
26.374
25.369
23.157
18
ppm

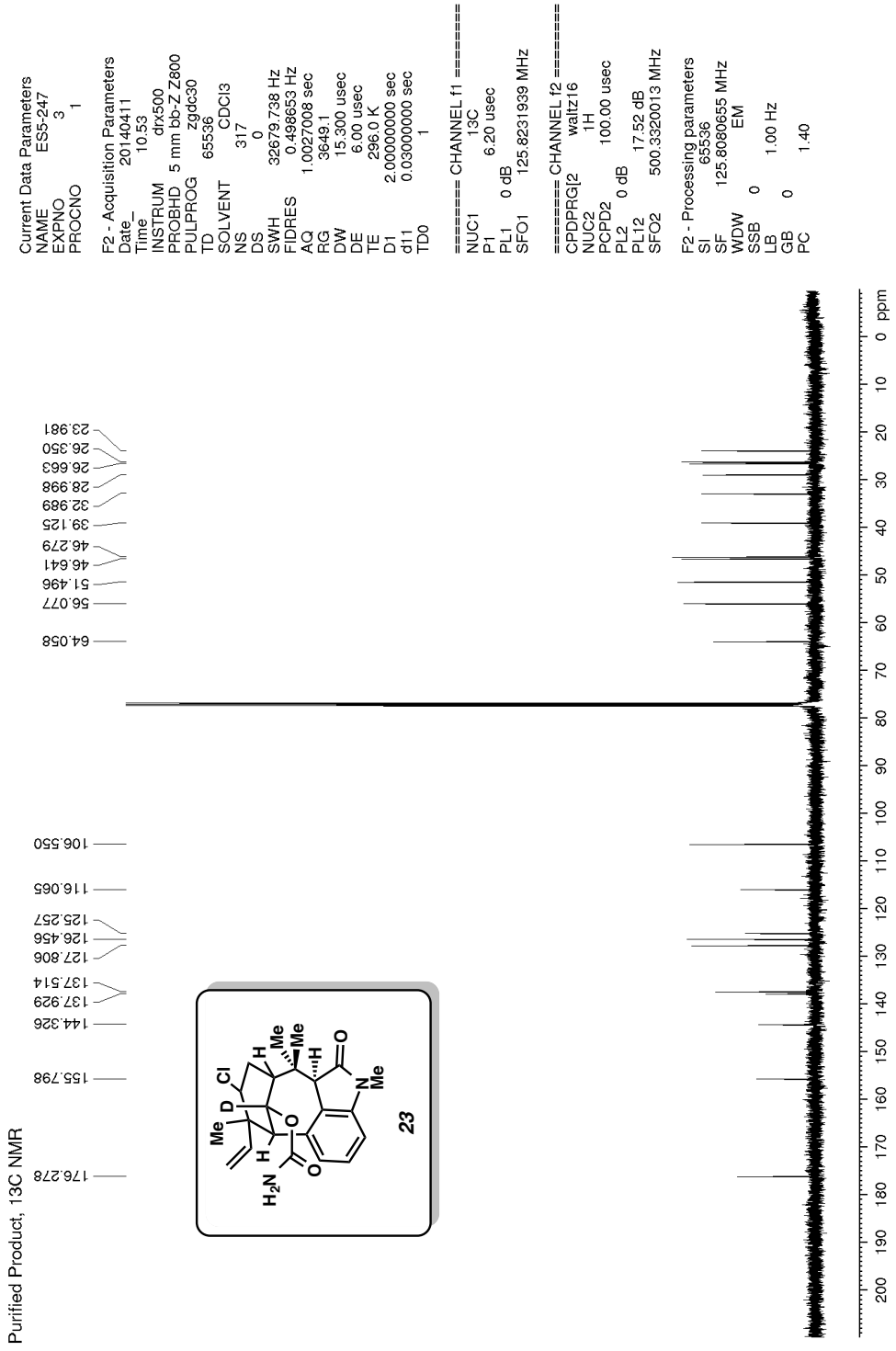

Purified Product, 13C NMR
Current Data Parameters
NAME NAW-2-152p
EXPNO 13
PROCNO 1
F2 - Acquisition Parameters
Date_ 20140623
Time 18.59
INSTRUM av500
PROBHD 5 mm DCH 13C-1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 80
DS 2
SWH 31250.000 Hz
FIDRES 0.476837 Hz
AQ 1.0485760 sec
RG 204.54
DW 16.000 usec
DE 18.00 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 125.7722511 MHz
NUC1 13C
P1 9.63 usec
PLW1 23.00000000 W
======== CHANNEL f2 ========
SFO2 500.1330008 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 13.50000000 W
PLW12 0.21094000 W
PLW13 0.13500001 W
F2 - Processing parameters
SI 131072
SF 125.7577728 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
22.758
25.888
26.112
26.376
31.318
39.523
50.462
51.635
53.834
57.542
61.752
69.610
107.529
124.832
125.057
128.885
133.784
144.913
175.753
200.288
Cl
Me
O
H
Me
Me
H
OH
O
N
Me
19
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

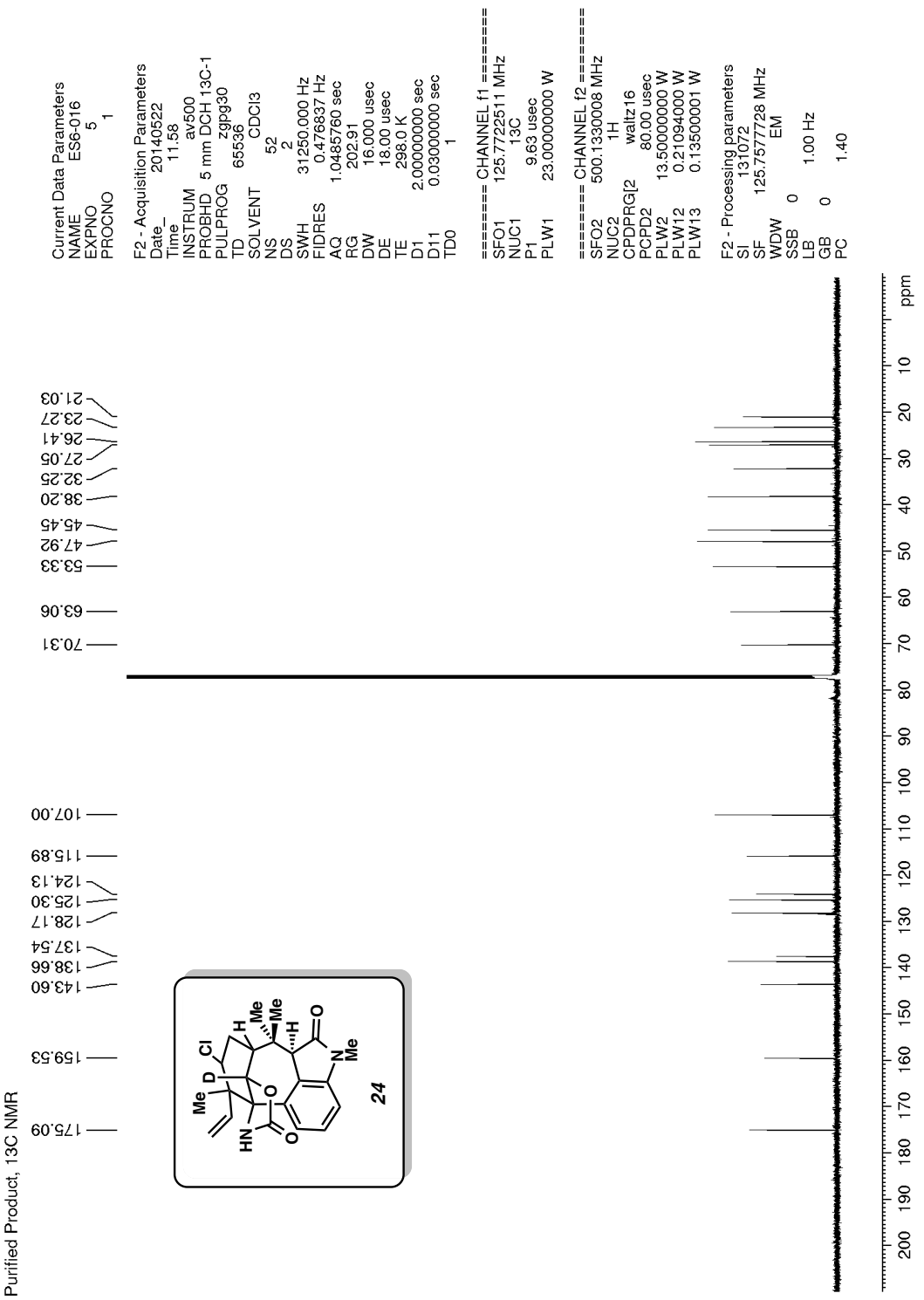

Purified Product, 13C NMR
Current Data Parameters
NAME NAW-2-171p
EXPNO 13
PROCNO 1
F2 - Acquisition Parameters
Date_ 20140723
Time_ 11.10
INSTRUM av500
PROBHD 5 mm DCH 13C-1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 24
DS 2
SWH 31250.000 Hz
FIDRES 0.476837 Hz
AQ 1.04857600 sec
RG 204.54
DW 16.000 usec
DE 18.00 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 125.7722511 MHz
NUC1 13C
P1 9.63 usec
PLW1 23.00000000 W
======== CHANNEL f2 ========
SFO2 500.1330008 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 13.50000000 W
PLW12 0.21094000 W
PLW13 0.13500001 W
F2 - Processing parameters
SI 131072
SF 125.7577732 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
176.23
144.45
138.64
138.27
128.03
125.45
124.42
115.01
106.29
69.98
65.26
60.70
54.77
50.58
44.39
39.71
31.45
29.66
26.33
25.93
22.59
7.10
4.93
Cl
Me
H
OR
H
Me
Me
O
N
Me
20, R = TES
ppm

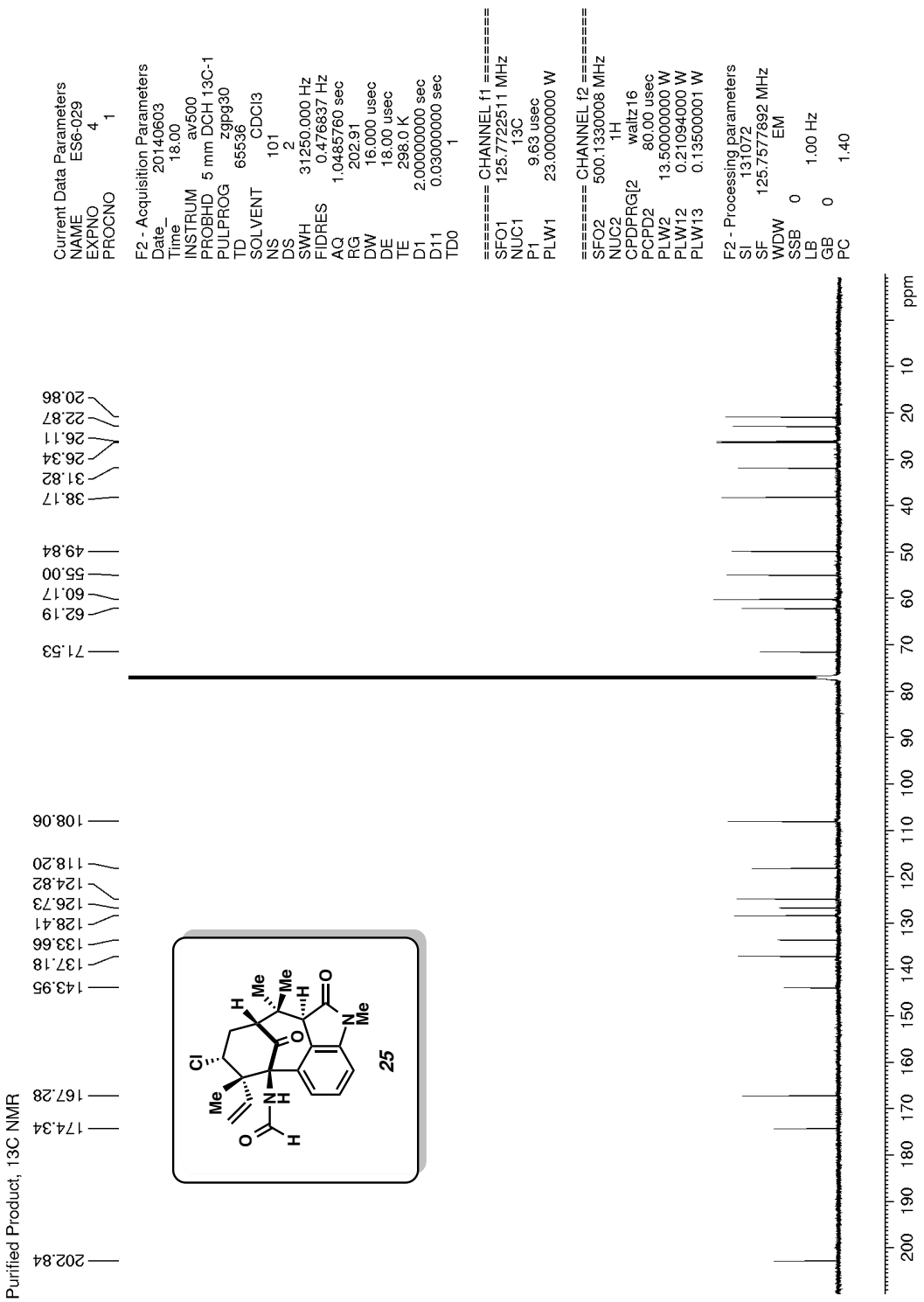

Purified Product, 13C NMR
Current Data Parameters
NAME NAW-2-174p
EXPNO 13
PROCNO 1
F2 - Acquisition Parameters
Date_ 20140728
Time 14.39
INSTRUM av500
PROBHD 5 mm DCH 13C-1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 80
DS 2
SWH 31250.000 Hz
FIDRES 0.476837 Hz
AQ 1.0485760 sec
RG 204.54
DW 16.000 usec
DE 18.00 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 125.7722511 MHz
NUC1 13C
P1 9.63 usec
PLW1 23.00000000 W
======== CHANNEL f2 ========
SFO2 500.1330008 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 13.50000000 W
PLW12 0.21094000 W
PLW13 0.13500001 W
F2 - Processing parameters
SI 131072
SF 125.7577720 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
175.916
155.273
144.508
137.942
137.047
128.206
125.747
124.354
115.617
106.659
73.153
64.619
56.965
51.121
50.727
44.085
39.718
30.999
29.401
26.387
25.662
22.257
Me Me
NMe
Me
Cl
H2N
8
ppm

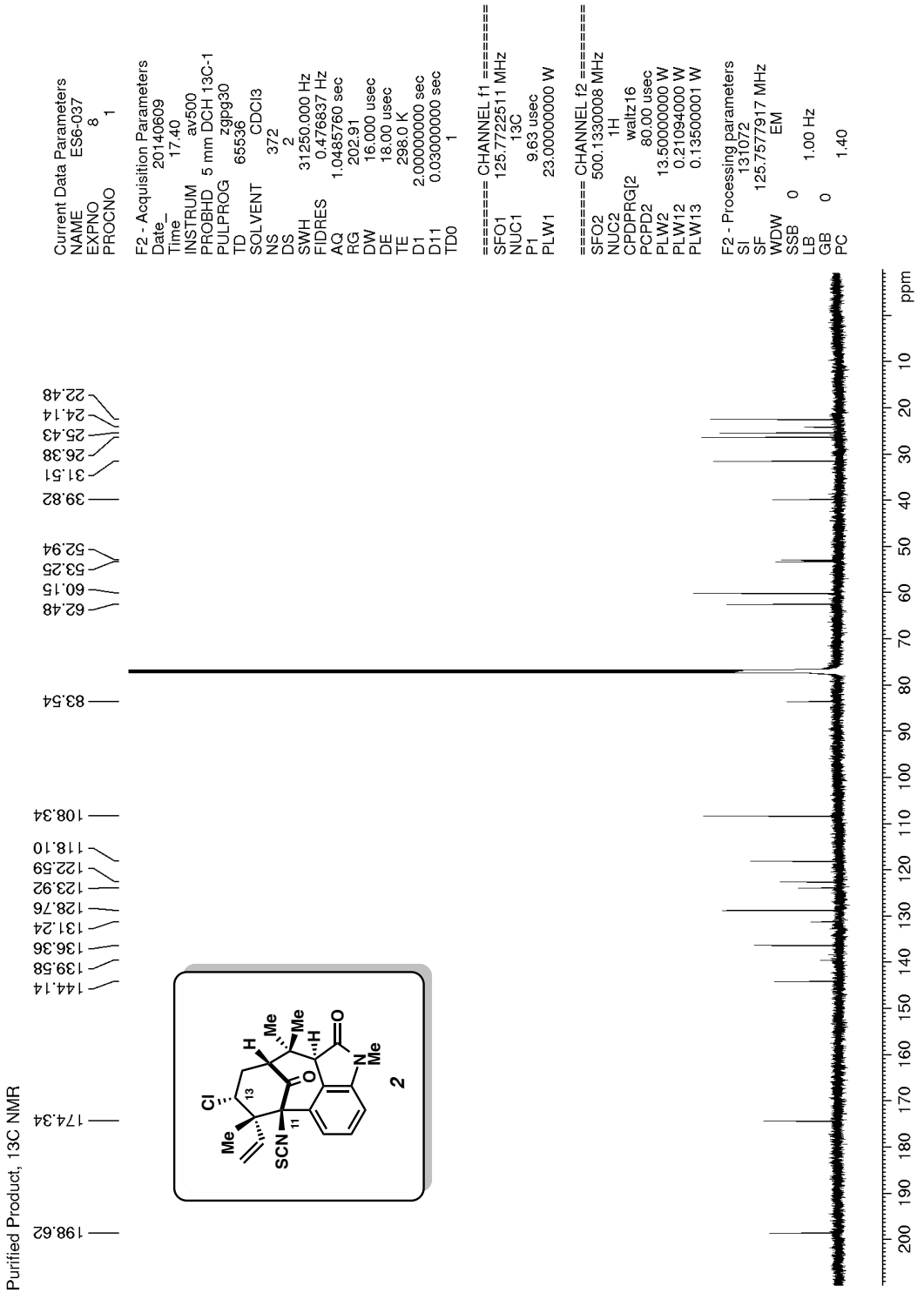

Purified Product, 13C NMR
174.21
158.00
144.71
137.90
136.42
128.69
126.67
123.04
115.95
107.27
78.71
67.46
61.69
53.56
52.65
44.38
41.26
40.19
28.32
26.51
21.12
17.75
Current Data Parameters
NAME NAW-2-147p
EXPNO 13
PROCNO 1
F2 - Acquisition Parameters
Date_ 20140718
Time_ 13.47
INSTRUM av500
PROBHD 5 mm DCH 13C-1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 80
DS 2
SWH 31250.000 Hz
FIDRES 0.476837 Hz
AQ 1.0485760 sec
RG 204.54
DW 16.000 usec
DE 18.00 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 125.7722511 MHz
NUC1 13C
P1 9.63 usec
PLW1 23.00000000 W
======== CHANNEL f2 ========
SFO2 500.1330008 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 13.50000000 W
PLW12 0.21094000 W
PLW13 0.13500001 W
F2 - Processing parameters
SI 131072
SF 125.7577723 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
21
ppm


Purified Product, 13C NMR
Current Data Parameters
NAME ES5-245
EXPNO 3
PROCNO 1
F2 - Acquisition Parameters
Date_ 20140410
Time_ 11.09
INSTRUM drx500
PROBHD 5 mm bb-Z Z800
PULPROG zgdc30
TD 65536
SOLVENT CDCl3
NS 300
DS 0
SWH 32679.738 Hz
FIDRES 0.498653 Hz
AQ 1.0027008 sec
RG 4096
DW 15.300 usec
DE 6.00 usec
TE 297.3 K
D1 2.00000000 sec
d11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 6.20 usec
PL1 0 dB
SFO1 125.8231939 MHz
======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 0 dB
PL12 17.52 dB
SFO2 500.3320013 MHz
F2 - Processing parameters
SI 65536
SF 125.8080650 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
22.152
25.011
26.463
29.722
32.640
41.820
48.554
50.859
62.491
64.475
68.943
107.251
117.948
124.412
125.166
129.026
132.144
136.221
144.620
175.344
207.586
ppm
22

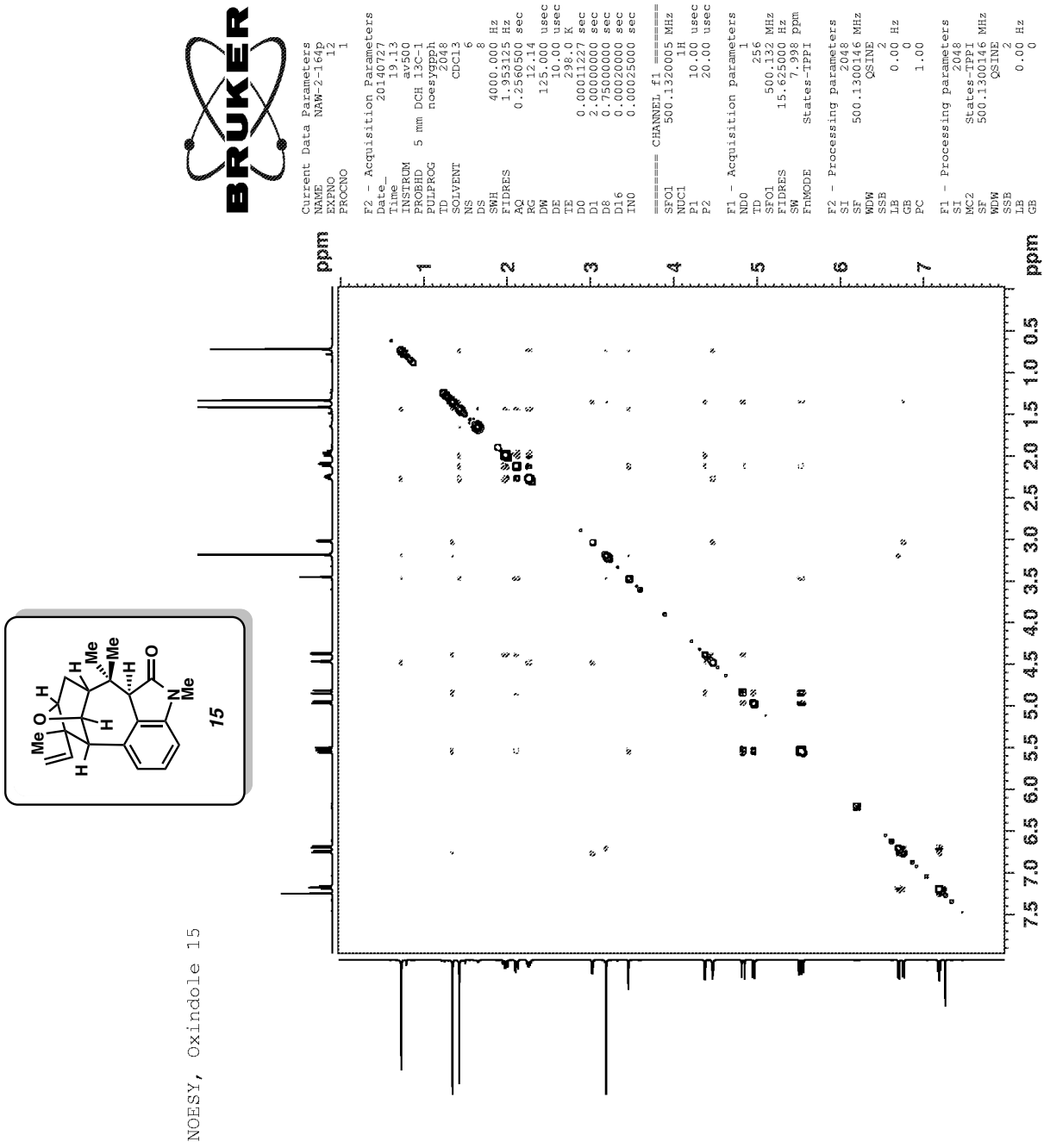

Purified Product, 13C NMR
Current Data Parameters
NAME ES5-247
EXPNO 3
PROCNO 1
F2 - Acquisition Parameters
Date_ 20140411
Time_ 10.53
INSTRUM drx500
PROBHD 5 mm bb-Z Z800
PULPROG zgdc30
TD 65536
SOLVENT CDCl3
NS 317
DS 0
SWH 32679.738 Hz
FIDRES 0.498653 Hz
AQ 1.0027008 sec
RG 3649.1
DW 15.300 usec
DE 6.00 usec
TE 296.0 K
D1 2.00000000 sec
d11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 6.20 usec
PL1 0 dB
SFO1 125.8231939 MHz
======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 0 dB
PL12 17.52 dB
SFO2 500.3320013 MHz
F2 - Processing parameters
SI 65536
SF 125.8080655 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
176.278
155.798
144.326
137.929
137.514
127.806
126.456
125.257
116.065
106.550
64.058
56.077
51.496
46.641
46.279
39.125
32.989
28.998
26.663
26.350
23.981
23
ppm


Purified Product, 13C NMR
Current Data Parameters
NAME ES6-016
EXPNO 5
PROCNO 1
F2 - Acquisition Parameters
Date_ 20140522
Time_ 11.58
INSTRUM av500
PROBHD 5 mm DCH 13C-1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 52
DS 2
SWH 31250.000 Hz
FIDRES 0.476837 Hz
AQ 1.0485760 sec
RG 202.91
DW 16.000 usec
DE 18.00 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 125.7722511 MHz
NUC1 13C
P1 9.63 usec
PLW1 23.00000000 W
======== CHANNEL f2 ========
SFO2 500.1330008 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 13.50000000 W
PLW12 0.21094000 W
PLW13 0.13500001 W
F2 - Processing parameters
SI 131072
SF 125.7577728 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
175.09
159.53
143.60
138.66
137.54
128.17
125.30
124.13
115.89
107.00
70.31
63.06
53.33
47.92
45.45
38.20
32.25
27.05
26.41
23.27
21.03
24
ppm


Purified Product, 13C NMR
Current Data Parameters
NAME ES6-029
EXPNO 4
PROCNO 1
F2 - Acquisition Parameters
Date_ 20140603
Time_ 18.00
INSTRUM av500
PROBHD 5 mm DCH 13C-1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 101
DS 2
SWH 31250.000 Hz
FIDRES 0.476837 Hz
AQ 1.0485760 sec
RG 202.91
DW 16.000 usec
DE 18.00 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 125.7722511 MHz
NUC1 13C
P1 9.63 usec
PLW1 23.00000000 W
======== CHANNEL f2 ========
SFO2 500.1330008 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 13.50000000 W
PLW12 0.21094000 W
PLW13 0.13500001 W
F2 - Processing parameters
SI 131072
SF 125.7577892 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
202.84
174.34
167.28
143.95
137.18
133.66
128.41
126.73
124.82
118.20
108.06
71.53
62.19
60.17
55.00
49.84
38.17
31.82
26.34
26.11
22.87
20.86
Me
Me
H
H
O
O
N
Me
Cl
Me
N
H
O
H
25
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


Purified Product, 13C NMR
198.62
174.34
144.14
139.58
136.36
131.24
128.76
123.92
122.59
118.10
108.34
83.54
62.48
60.15
53.25
52.94
39.82
31.51
26.38
25.43
24.14
22.48
Current Data Parameters
NAME ES6-037
EXPNO 8
PROCNO 1
F2 - Acquisition Parameters
Date_ 20140609
Time_ 17.40
INSTRUM av500
PROBHD 5 mm DCH 13C-1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 372
DS 2
SWH 31250.000 Hz
FIDRES 0.476837 Hz
AQ 1.0485760 sec
RG 202.91
DW 16.000 usec
DE 18.00 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 125.7722511 MHz
NUC1 13C
P1 9.63 usec
PLW1 23.00000000 W
======== CHANNEL f2 ========
SFO2 500.1330008 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 13.50000000 W
PLW12 0.21094000 W
PLW13 0.13500001 W
F2 - Processing parameters
SI 131072
SF 125.7577917 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
Cl
Me
SCN
H
Me
Me
H
O
O
N
Me
13
11
2
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

2-Dimensional NMR Spectrum for Oxindole 15:


NOESY, Oxindole 15
15
Current Data Parameters
NAME NAW-2-164p
EXPNO 12
PROCNO 1
F2 - Acquisition Parameters
Date_ 20140727
Time_ 19.13
INSTRUM av500
PROBHD 5 mm DCH 13C-1
PULPROG noesygppph
TD 2048
SOLVENT CDCl3
NS 8
DS 8
SWH 4000.000 Hz
FIDRES 1.953125 Hz
AQ 0.2560500 sec
RG 12.14
DW 125.000 usec
DE 10.00 usec
TE 298.0 K
D0 0.00011227 sec
D1 2.00000000 sec
D8 0.75000000 sec
D16 0.00020000 sec
IN0 0.00025000 sec
======== CHANNEL f1 ========
SFO1 500.1320005 MHz
NUC1 1H
P1 10.00 usec
P2 20.00 usec
F1 - Acquisition parameters
ND0 1
TD 256
SFO1 500.132 MHz
FIDRES 15.625000 Hz
SW 7.998 ppm
FnMODE States-TPPI
F2 - Processing parameters
SI 2048
SF 500.1300146 MHz
WDW QSINE
SSB 2
LB 0.00 Hz
GB 0
PC 1.00
F1 - Processing parameters
SI 2048
MC2 States-TPPI
SF 500.1300146 MHz
WDW QSINE
SSB 2
LB 0.00 Hz
GB 0
ppm
ppm