

Concise Enantiospecific Total Synthesis of Tubingensin A

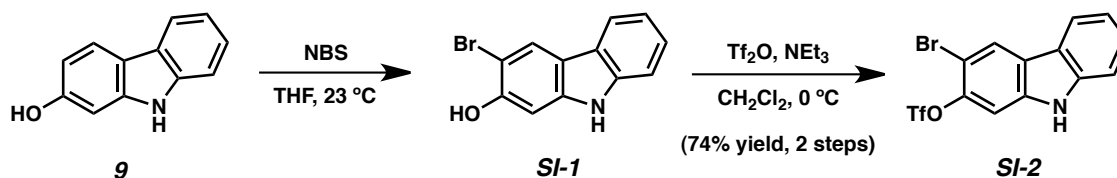
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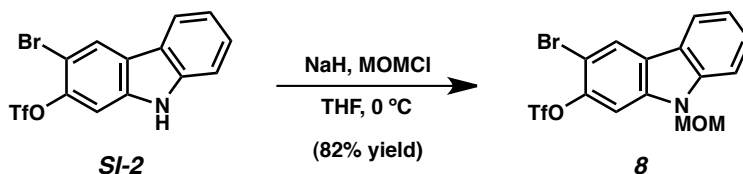
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Materials and Methods. Unless stated otherwise, reactions were conducted in flame-dried glassware under an atmosphere of nitrogen using anhydrous solvents (either freshly distilled or passed through activated alumina columns). All commercially obtained reagents were used as received unless otherwise specified. The following reagents were distilled prior to use: chlorotrimethylsilane (TMSCl, distilled over CaH₂), chlorotriethylsilane (TESCl, distilled over CaH₂), chlorodimethylisopropylsilane (DMIPSCl), hexamethylphosphoramide (HMPA, distilled over CaH₂ and stored over 4 Å molecular sieves), trifluoromethanesulfonic anhydride (Tf₂O), isopropyl alcohol (*i*-PrOH, distilled over CaO after refluxing overnight). 2-Iodoxybenzoic acid (IBX) was prepared following the procedure reported by Frigerio et al.¹ Prenyl tri(*n*-butyl)stannane was prepared using prenyl bromide according to the general procedure of Keck et al. and distilled prior to use.² Methyl iodide (MeI) was passed over basic Brockman Grade I 58 Å activated alumina immediately prior to use. 18-Crown-6 was recrystallized from acetonitrile and stored in a glovebox. *N,N*-Dimethylmethyleneiminium iodide was purchased from Sigma–Aldrich and stored inside a glovebox. Pd(PPh₃)₄ was purchased from Strem and stored inside a glovebox at –20 °C. Karstedt’s catalyst was purchased as a 2% solution in xylene from Sigma–Aldrich and stored inside a glovebox. Reaction temperatures were controlled using an IKA Mag temperature modulator, and 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, vanillin, ninhydrin, and potassium permanganate staining. Silicycle Siliaflash P60 (particle size 0.040–0.063 mm), was used for flash column chromatography. ¹H NMR and 2D-NMR spectra were recorded on Bruker spectrometers (at 300 MHz or 500 MHz) and are reported relative to deuterated solvent signals. Data for ¹H NMR spectra are reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz), and integration. ¹³C NMR spectra were recorded on Bruker Spectrometers (at 75 or 125 MHz). Data for ¹³C NMR spectra are reported in terms of chemical shift, and when necessary, multiplicity, coupling constant (Hz) and carbon type. IR spectra were recorded on a Perkin-Elmer 100 spectrometer and are reported in terms of frequency of absorption (cm⁻¹). High resolution mass spectra were obtained from the UC Irvine Mass Spectrometry Facility and the UCLA Molecular Instrumentation Center. Melting points were determined using a DigiMelt MPA160 melting point apparatus. Images in Figure 1 and Scheme 5 were created using CYLview.³

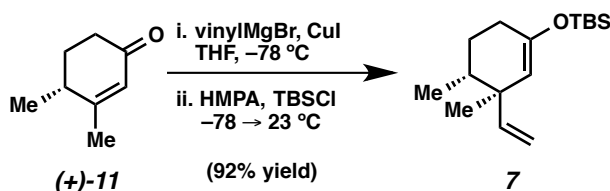
Experimental Procedures.

Bromotriflate SI-2. Known compound **SI-1** was prepared using a modification of the procedure reported by Erra–Balsells.⁴ To a mixture of 2-hydroxycarbazole (**9**, 3.50 g, 19.10 mmol, 1 equiv) in THF (110 mL) was added NBS (3.63 g, 20.40 mmol, 1.07 equiv) as a solution in THF (90 mL) over 13 min. After stirring for 10 min, silica gel (~30 mL) was added and the mixture was concentrated under reduced pressure. The resulting material was loaded onto a column and purified by flash chromatography (4:1:1 Benzene:CH₂Cl₂:Et₂O) to provide **SI-1** as an off-white solid. Spectral data match those previously reported.⁴ All material was carried on to the subsequent triflation step.

To a suspension of **SI-1** in CH₂Cl₂ (210 mL) was added NEt₃ (8.0 mL, 57.56 mmol, 3 equiv) and the reaction was cooled to 0 °C. Triflic anhydride (3.5 mL, 20.84 mmol, 1.1 equiv) was added dropwise over 3 min. The reaction was stirred for 25 min, quenched with sat. aq. NaHCO₃ (125 mL) and then allowed to warm to room temperature. The layers were separated and the aqueous layer was extracted with CH₂Cl₂ (2 x 75 mL). The combined organic layers were dried over MgSO₄. Evaporation under reduced pressure afforded crude product, which was further purified by flash chromatography (6:1 Hexanes:EtOAc) to provide **SI-2** (5.59 g, 74% yield, 2 steps) as a white solid. Mp: 124–126 °C; R_f 0.27 (6:1 Hexanes:EtOAc); ¹H NMR (500 MHz, C₆D₆): δ 7.83 (s, 1H), 7.56 (d, *J* = 7.9, 1H), 7.28 (app. t, *J* = 7.7, 1H), 7.09 (app. t, *J* = 7.6, 1H), 6.91 (dd, *J* = 8.1, 0.8, 1H), 6.89 (s, 1H), 6.26 (br s, 1H); ¹³C NMR (125 MHz, C₆D₆): δ 144.4, 140.7, 138.1, 127.3, 125.2, 124.3, 121.6, 121.1, 120.8, 119.5 (q, *J* = 321 Hz, CF₃), 111.0, 105.3, 105.2; IR (film): 3376, 1605, 1429, 1209, 1130 cm⁻¹; HRMS-ESI (*m/z*) [M – H]⁻ calcd for C₁₃H₆BrF₃NO₃S, 391.9204; found, 391.9204.

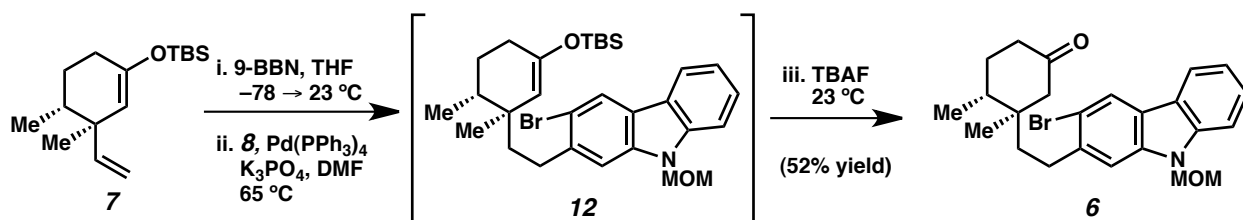


***N*-MOM-Carbazole 8.** To a solution of carbazole **SI-2** (7.11 g, 18.04 mmol, 1 equiv) in THF (100 mL) at 0 °C was added NaH (60% dispersion in mineral oil, 941.2 mg, 23.53 mmol, 1.3 equiv) in two portions. (*Caution: The reaction is exothermic and releases hydrogen gas. Make sure that the reaction is cooled and is properly ventilated to prevent pressure buildup*). After 10 min, MOMCl (1.8 mL, 23.70 mmol, 1.3 equiv) was added dropwise over 1 min. The reaction was stirred for 20 min, quenched with H₂O (150 mL) and diluted with CH₂Cl₂ (150 mL). The layers were separated, and the aqueous layer was extracted with CH₂Cl₂ (2 x 100 mL). The combined organic layers were dried over MgSO₄. Evaporation under reduced pressure afforded the crude product, which was purified by flash chromatography (3:1 Hexanes:Et₂O) to provide **8** (6.49 g, 82% yield) as a white solid. Mp: 84–86 °C; R_f 0.37 (3:1 Hexanes:Et₂O); ¹H NMR (500 MHz, CDCl₃): δ 8.32 (s, 1H), 8.04 (d, *J* = 7.8, 1H), 7.59–7.51 (m, 3H), 7.34 (ddd, *J* = 8.0, 5.5, 2.5, 1H), 5.65 (s, 2H), 3.30 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 144.6, 141.8, 139.4, 127.7, 125.1, 124.5, 121.5, 121.3, 120.9, 118.9 (q, *J* = 321, CF₃), 109.7, 106.3, 104.3, 74.5, 56.5; IR (film): 2927, 1596, 1420, 1208, 1130, 1113 cm⁻¹; HRMS-ESI (*m/z*) [M + NH₄]⁺ calcd for C₁₅H₁₅BrF₃N₂O₄S, 454.98825; found, 454.98625.



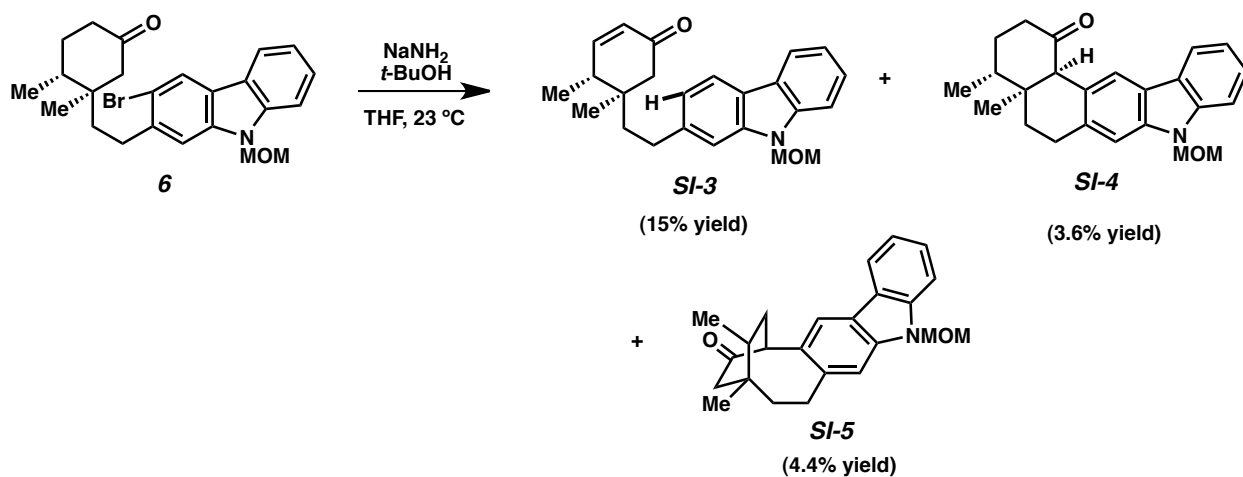
Silyl Enol Ether 7. To a flask charged with CuI (1.53 g, 8.052 mmol, 2 equiv) was added THF (50 mL). The mixture was cooled to –78 °C and vinyl magnesium bromide (1.0 M in THF, 16.1 mL, 16.10 mmol, 4 equiv) was added dropwise over 10 min. The reaction was warmed to –10 °C for 25 min, then re-cooled to –78 °C. Enone **(+)-11** (500 mg, 4.026 mmol, 1 equiv) was added dropwise over 10 min as a solution in THF (11 mL). HMPA (11.2 mL, 64.42 mmol, 16 equiv)

and TBSCl (1.27 g, 8.46 mmol, 2.1 equiv) were then added to the reaction mixture as a solution in THF (6 mL). The reaction was warmed to room temperature and stirred overnight. The reaction was quenched with H₂O (30 mL) and diluted with Et₂O (30 mL). The layers were separated and the aqueous layer was filtered over celite, which was washed with Et₂O (300 mL). The combined organic layers were washed with brine (30 mL) and the resulting aqueous layer was extracted with Et₂O (2 x 20 mL). The combined organic layer was dried over MgSO₄ and concentrated under reduced pressure. The crude product was purified via flash chromatography (19:1 Hexanes: NEt₃) to afford **7** (982 mg, 92% yield) as a yellow oil. R_f 0.55 (Hexanes); ¹H NMR (500 MHz, C₆D₆): δ 5.80 (dd, *J* = 17.4, 10.5, 1H), 5.06 (dd, *J* = 17.4, 1.6, 1H), 5.00 (dd, *J* = 10.5, 1.6, 1H), 4.77 (s, 1H), 1.92–2.09 (m, 2H), 1.35–1.51 (m, 3H), 0.99 (s, 9H), 0.97 (s, 3H), 0.82 (d, *J* = 6.5, 3H), 0.150 (s, 3H), 0.147 (s, 3H); ¹³C NMR (125 MHz, C₆D₆): δ 150.5, 149.1, 112.7, 111.7, 41.6, 36.9, 29.6, 27.3, 25.9, 21.1, 18.3, 15.6, –4.17, –4.26; IR (thin film) 2929, 2858, 1663, 1363, 1192 cm⁻¹. HRMS-ESI (*m/z*) [M + H]⁺ calcd for C₁₆H₃₁OSi, 267.2144; found 267.2131. [α]_D²³ –19.3° (*c* = 0.10, EtOAc).



Ketone 6. A vial charged with silyl enol ether **7** (50.0 mg, 0.188 mmol, 2 equiv) was cooled to –78 °C. 9-BBN (0.5 M in THF, 0.43 mL, 0.216 mmol, 2.3 equiv) was then added dropwise. The reaction was allowed to warm to room temperature and stirred for 5 h. To a separate vial was added Pd(PPh₃)₄ (22.0 mg, 0.019 mmol, 0.2 equiv) in the glovebox. The vial was removed, DMF (0.38 mL) was added, and the solution was sparged with N₂ for 10 min. K₃PO₄ (29.9 mg, 0.141 mmol, 1.5 equiv) and carbazole **8** (41.2 mg, 0.094 mmol, 1 equiv) were then added to the DMF solution. The THF solution was then added to the DMF mixture and the reaction was heated to 65 °C for 24 h. The reaction was cooled to room temperature and TBAF (1.0 M in THF, 0.47 mL, 0.47 mmol, 5 equiv) was added. After stirring for 20 min, the reaction was quenched with brine (5 mL) and EtOAc (5 mL). The layers were separated and the aqueous layer was extracted

with EtOAc (3 x 5 mL). The combined organic layers were dried over MgSO₄, and concentrated under reduced pressure. The compound was purified by flash chromatography (4:1 Hexanes:EtOAc) to afford **6** (21.8 mg, 52% yield) as a clear oil. R_f 0.39 (2:1 hexanes:EtOAc); ¹H NMR (500 MHz, CDCl₃): d 8.21 (s, 1H), 7.99 (app. d, *J* = 7.6, 1H), 7.51 (d, *J* = 8.2, 1H), 7.47 (ddd, *J* = 8.3, 7.0, 1.2, 1H), 7.35 (s, 1H), 7.27 (ddd, *J* = 8.2, 7.1, 1.2, 1H), 5.65 (s, 2H), 3.29 (s, 3H), 2.87 (m, 2H), 2.53 (d, *J* = 13.2, 1H), 2.37–2.39 (m, 2H), 2.28 (d, *J* = 13.2, 1H), 1.92–2.00 (m, 2H), 1.59–1.76 (m, 3H), 1.02 (d, *J* = 7.3, 3H), 0.89 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): 212.5, 141.2, 140.2, 139.3, 126.6, 124.5, 123.7, 122.5, 120.53, 120.51, 115.4, 110.6, 109.4, 74.4, 56.3, 52.4, 42.8, 41.13, 41.09, 37.1, 31.5, 30.9, 19.1, 15.2; IR (thin film): 2957, 1708, 1602, 1451, 1241 cm⁻¹; HRMS-ESI (*m/z*) [M + Na]⁺ calcd for C₂₄H₂₈BrNO₂Na, 464.1201; found 464.1188. [α]_D²³ +12.0° (*c* = 0.10, CHCl₃).

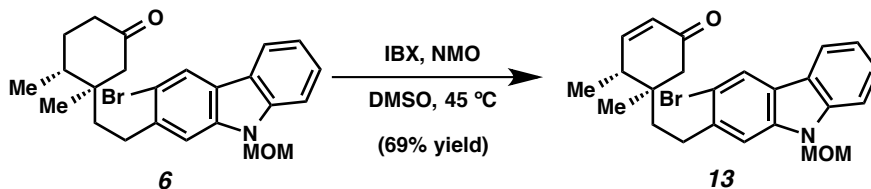
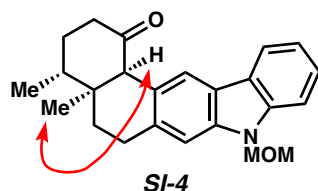


Aryne products SI-3, SI-4, and SI-5. To a vial inside the glovebox was added NaNH₂ (44.5 mg, 1.14 mmol, 10.7 equiv) and the solid was crushed into a powder. The vial was removed from the glovebox and THF (2.1 mL) was added, followed by *t*-BuOH (36.5 μL, 0.382 mmol, 3.6 equiv). The vial was placed in a heating block at 40 °C and stirred for 1 h. After cooling to room temperature under N₂, ketone **6** (47.4 mg, 0.107 mmol, 1 equiv) was added as a solution in THF (1.5 mL). The vial containing **6** was then washed with additional THF (600 μL) and the resulting solution was added to the reaction mixture. The resulting solution was stirred at 23 °C for 3 h, then quenched with H₂O (1 mL) and diluted with EtOAc (10 mL), and sat. aq. NH₄Cl (3 mL).

The layers were separated, and the aqueous layer extracted with EtOAc (2 x 10 mL). The combined organic layers were dried over MgSO₄ and concentrated under reduced pressure to afford the crude products. The crude material was further purified by preparative thin layer chromatography (2:1 Hexanes:EtOAc) to afford compounds **SI-3** (5.8 mg, 15% yield), **SI-4** (1.4 mg, 3.6% yield), and **SI-5** (1.7 mg, 4.4% yield) as colorless oils. **SI-3**: R_f 0.29 (2:1 Hexanes:EtOAc); ¹H NMR (500 MHz, CDCl₃): δ 8.04 (d, *J* = 7.8, 1H), 7.98 (d, *J* = 8.0, 1H), 7.53 (d, *J* = 8.2, 1H), 7.44 (ddd, *J* = 8.2, 7.2, 1.1, 1H), 7.32 (s, 1H), 7.28–7.24 (m, 1H), 7.09 (dd, *J* = 8.0, 1.2, 1H), 6.68 (dd, *J* = 10.1, 3.0, 1H), 6.01 (dd, *J* = 10.1, 2.4, 1H), 5.68 (s, 2H), 3.31 (s, 3H), 2.83–2.71 (m, 2H), 2.63–2.56 (m, 1H), 2.48 (d, *J* = 15.8, 1H), 2.42 (d, *J* = 15.8, 1H), 1.87–1.74 (m, 2H), 1.14 (d, *J* = 7.5, 3H), 1.01 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 200.1, 154.8, 141.1, 141.0, 140.9, 128.1, 125.8, 123.6, 121.8, 120.9, 120.5, 120.3, 120.1, 109.2, 108.9, 74.3, 56.3, 48.9, 43.5, 39.8, 39.3, 31.2, 20.2, 14.4; IR (film): 2932, 1675, 1604, 1460, 1326, 1065 cm⁻¹; HRMS-ESI (*m/z*) [M + NH₄]⁺ calcd for C₂₄H₃₁N₂O₂, 379.23800; found, 379.23730; [α]_D²³ -16.7° (*c* = 0.10, CHCl₃). **SI-4**: R_f 0.53 (2:1 Hexanes:EtOAc); ¹H NMR (500 MHz, CDCl₃): δ 7.97 (app. d, *J* = 7.8, 1H), 7.56 (s, 1H), 7.49 (app. d, *J* = 8.0, 1H), 7.43 (ddd, *J* = 8.2, 7.1, 1.1, 1H), 7.32 (s, 1H), 7.23 (ddd, *J* = 7.9, 7.0, 0.9, 1H), 5.64 (s, 2H), 3.53 (bs, 1H), 3.31 (s, 3H), 3.15 (m, 1H), 3.00 (dd, *J* = 17.6, 4.3, 1H), 2.52 (m, 1H), 2.29 (m, 1H), 2.11 (m, 1H), 2.02 (ddd, *J* = 13.8, 5.7, 2.1, 1H), 1.74 (m, 2H), 1.53 (m, 1H), 1.00 (s, 3H), 0.96 (d, *J* = 6.4, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 214.6, 141.2, 139.9, 133.8, 126.1, 125.4, 123.4, 122.8, 120.5, 120.2, 119.3, 109.6, 109.1, 74.4, 63.0, 56.3, 39.0, 38.9, 33.7, 31.2, 30.1, 26.4, 21.1, 14.8; IR (film): 2922, 2855, 1702, 1462, 1240, 1065 cm⁻¹; HRMS-ESI (*m/z*) [M + NH₄]⁺ calcd for C₂₄H₃₁N₂O₂, 379.23800; found, 379.23720; [α]_D²³ +27.3° (*c* = 0.10, CHCl₃). **SI-5**: R_f 0.42 (2:1 Hexanes:EtOAc); ¹H NMR (500 MHz, CDCl₃): δ 8.01 (app. d, *J* = 7.9, 1H), 7.78 (s, 1H), 7.51 (app. d, *J* = 8.5, 1H), 7.44 (ddd, *J* = 8.2, 7.2, 1.1, 1H), 7.25 (app. t, *J* = 7.1, 1H), 7.22 (s, 1H), 5.64 (d, *J* = 1.2, 2H), 3.95 (app. t, *J* = 3.1, 1H), 3.30 (s, 3H), 3.04 (ddd, *J* = 16.0, 13.3, 3.8, 1H), 2.80 (dt, *J* = 16.0, 4.0, 1H), 2.55 (d, *J* = 17.2, 1H), 2.32 (d, *J* = 17.2, 1H), 1.89 (m, 3H), 1.81 (m, 1H), 1.70 (m, 1H), 1.03 (s, 3H), 0.91 (d, *J* = 7.1, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 217.4, 141.1, 139.9, 137.7, 132.8, 126.0, 123.2, 122.6, 122.0, 120.3, 120.1, 110.8, 109.3, 74.4, 56.3, 56.0, 49.6, 48.7, 41.1, 35.2, 34.4, 32.0, 28.7,

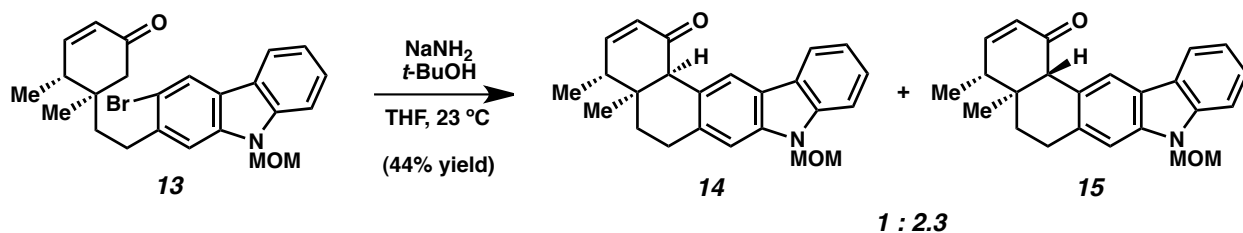
18.4; IR (film): 2920, 2848, 1709, 1473, 1238, 1065 cm^{-1} ; HRMS-ESI (m/z) $[\text{M} + \text{NH}_4]^+$ calcd for $\text{C}_{24}\text{H}_{31}\text{N}_2\text{O}_2$, 379.23800; found, 379.23724; $[\alpha]_D^{23} +50.0^\circ$ ($c = 0.10$, CHCl_3).

The stereochemistry of decalin **SI-4** was verified by NOESY (500MHz, CDCl_3), as the following correlation was observed:



Enone 13. Note: The reaction shown here was found to give variable yields when carried out on larger scale. Two separate vials were each charged with IBX¹ (372.2 mg, 1.33 mmol, 2.5 equiv), *N*-methylmorpholine-*N*-oxide (160.9 mg, 1.37 mmol, 2.6 equiv) and DMSO (1.8 mL). The vials were capped and heated to 45 °C. After stirring for 15 min, during which time the IBX mixture became homogenous. The IBX solutions were transferred to two vials each of which had been charged with ketone **6** (234.2 mg, 0.529 mmol, 1 equiv). The vials were heated to 45 °C for 19 h. The reactions were cooled to room temperature and quenched with a 1:1 mixture of sat. aq. NaHCO_3 :sat. aq. $\text{Na}_2\text{S}_2\text{O}_3$ (1.5 mL each), combined, and further diluted with EtOAc (40 mL), and H_2O (13 mL). The layers were separated and the aq. layer was extracted with EtOAc (3 x 30 mL). The combined organic layers were dried over MgSO_4 . Evaporation under reduced pressure afforded the crude product which was purified by flash chromatography (2:1 Hexanes:EtOAc) to give **13** as a white, amorphous solid (321.8 mg, 69% yield). R_f 0.32 (2:1 Hexanes:EtOAc); ^1H NMR (500 MHz, CDCl_3): δ 8.21 (s, 1H), 7.99 (ddd, $J = 7.8, 1.2, 0.8$, 1H), 7.52 (app. dt, $J = 8.2, 0.9$, 1H), 7.47, (ddd, $J = 8.2, 7.0, 1.2$, 1H), 7.36 (s, 1H), 7.27 (ddd, $J = 7.9, 6.9, 1.0$, 1H), 6.70

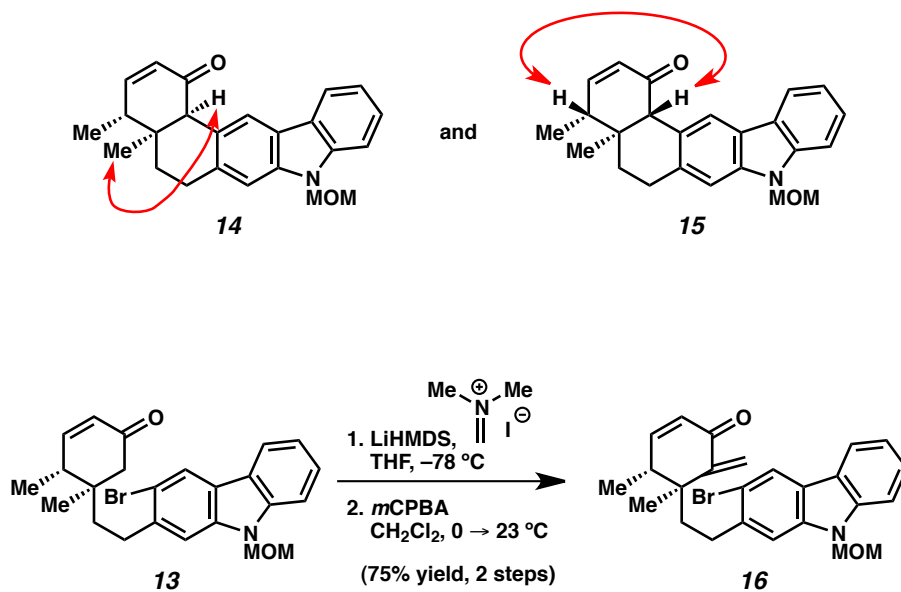
(dd, $J = 10.1, 3.0, 1\text{H}$), 6.02, (dd, $J = 10.1, 2.5, 1\text{H}$), 5.65 (s, 2H), 3.29 (s, 3H), 2.93–2.81 (m, 2H), 2.63 (app. ddt, $J = 14.8, 7.4, 2.8, 1\text{H}$), 2.53 (d, $J = 15.8, 1\text{H}$), 2.46 ($J = 15.8, 1\text{H}$), 1.82–1.69 (m, 2H), 1.16 (d, $J = 7.4, 3\text{H}$), 1.03 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3): (23 of 24 C) δ 200.2, 154.8, 141.2, 140.2, 139.0, 128.1, 126.6, 124.5, 123.7, 122.5, 120.5, 115.4, 110.6, 109.4, 74.3, 56.3, 49.0, 41.8, 39.9, 39.1, 32.0, 20.1, 14.5; IR (film): 2956, 1673, 1453, 1241, 1110 cm^{-1} ; HRMS-ESI (m/z) $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{24}\text{H}_{26}\text{BrNO}_2\text{Na}$, 462.1045; found, 462.1045. $[\alpha]_D^{23} -6.8^\circ$ ($c = 1.0, \text{CHCl}_3$).



Cyclized products 14 and 15. To a vial inside the glovebox was added NaNH_2 (40.9 mg, 1.05 mmol, 10.3 equiv) and the solid was crushed into a powder. The vial was removed from the glovebox and THF (1.6 mL) added, followed by $t\text{-BuOH}$ (35 μL , 0.366 mmol, 3.6 equiv). The vial was placed in a heating block at 40 $^\circ\text{C}$ and stirred for 1 h. After cooling to room temperature under N_2 , enone **13** (44.8 mg, 0.105 mmol, 1 equiv) was added as a solution in THF (1.2 mL). The vial containing **13** was then washed with additional THF (400 μL) and the resulting solution was added to the reaction mixture. The resulting solution was stirred at 23 $^\circ\text{C}$ for 3 h, then quenched with H_2O (2 mL) and diluted with EtOAc (10 mL), and sat. aq. NH_4Cl (1 mL). The layers were separated, and the aqueous layer extracted with EtOAc (3 x 10 mL). The combined organic layers were dried over MgSO_4 and concentrated under reduced pressure to afford the crude products. The crude material was further purified by preparative thin layer chromatography (3:2 Hexanes:EtOAc) to afford compounds **14** and **15** (16.1 mg, 44% yield) as an inseparable mixture of diastereomers (1 : 2.3 ratio of **14** : **15**). These compounds were characterized as a mixture. R_f 0.51 (3:2 Hexanes:EtOAc); **15**(major): ^1H NMR (500 MHz, CDCl_3): δ 8.33 (s, 1H), 8.07 (d, $J = 7.8, 1\text{H}$), 7.48 (d, $J = 8.2, 1\text{H}$), 7.44–7.40 (m, 1H), 7.27 (s, 1H), 7.25–7.21 (m, 1H), 6.52 (dd, $J = 10.1, 1.9, 1\text{H}$), 6.17 (dd, $J = 10.0, 3.2, 1\text{H}$), 5.64 (s, 2H),

4.00 (s, 1H), 3.29 (s, 3H), 3.23–3.05 (m, 1H), 2.95 (ddd, $J = 17.1, 5.2, 2.0$, 1H), 2.75–2.64 (m, 1H), 2.09–2.02 (m, 1H), 1.78 (td, $J = 13.0, 5.3$, 1H), 1.17 (d, $J = 7.5$, 3H), 0.86 (s, 3H); **14**(minor): ^1H NMR (500 MHz, CDCl_3): δ 8.00 (d, $J = 7.7$, 1H), 7.72 (s, 1H), 7.47 (d, $J = 8.0$, 1H), 7.44–7.40 (m, 1H), 7.30 (s, 1H), 7.25–7.21 (m, 1H), 6.49 (dd, $J = 10.1, 2.3$, 1H), 6.06 (dd, $J = 10.0, 2.9$, 1H), 5.62 (s, 2H), 3.49 (s, 1H), 3.30 (s, 3H), 3.23–3.05 (m, 2H), 2.75–2.64 (m, 1H), 2.09–2.02 (m, 1H), 1.69–1.62 (m, 1H), 1.13 (d, $J = 7.5$, 3H), 1.08 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3): δ 200.9, 199.6, 154.3, 150.6, 141.20, 141.15, 140.0, 139.7, 134.8, 133.8, 130.0, 127.3, 125.9, 125.7, 124.0, 123.6, 123.3, 123.2, 122.7, 122.5, 122.2, 120.61, 120.58, 120.1, 120.0, 119.7, 109.4, 109.0, 108.9, 108.7, 74.32, 74.26, 59.2, 56.7, 56.3, 56.2, 44.6, 41.8, 39.4, 34.4, 33.4, 32.8, 26.92, 26.87, 21.8, 14.0, 13.8, 12.5; IR (film): 2966, 2930, 1685, 1671, 1473, 1460, 1330, 1239, 1062 cm^{-1} ; HRMS-ESI (m/z) [$M - \text{H}$] $^-$ calcd for $\text{C}_{24}\text{H}_{24}\text{NO}_2$, 358.18125; found, 358.18067.

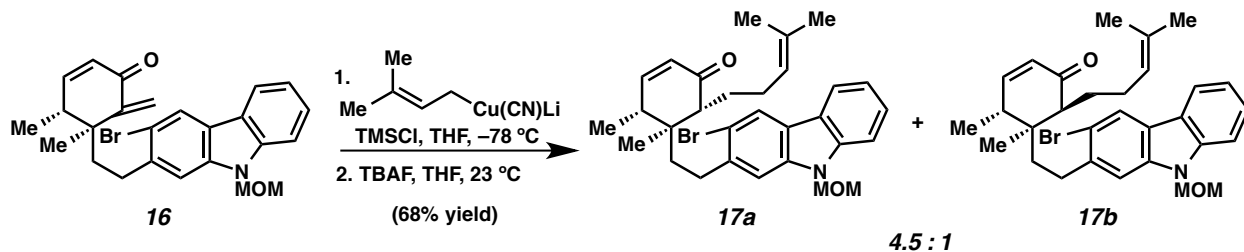
The relative stereochemistry of **14** and **15** was verified by NOESY (500MHz, CDCl_3), as the following correlations were observed:



Dienone 16. To a solution of enone **13** (245.9 mg, 0.558 mmol, 1 equiv) in THF (1.9 mL) at $-78\text{ }^{\circ}\text{C}$ was added LiHMDS (148.3 mg, 0.886 mmol, 1.6 equiv) as a solution in THF (1.5 mL). After 10 min, the enolate mixture was warmed to room temperature over 10 min. In a separate flask, Eschenmoser's salt (207.1 mg, 1.12 mmol, 2 equiv) was suspended in THF (1.5 mL) and cooled

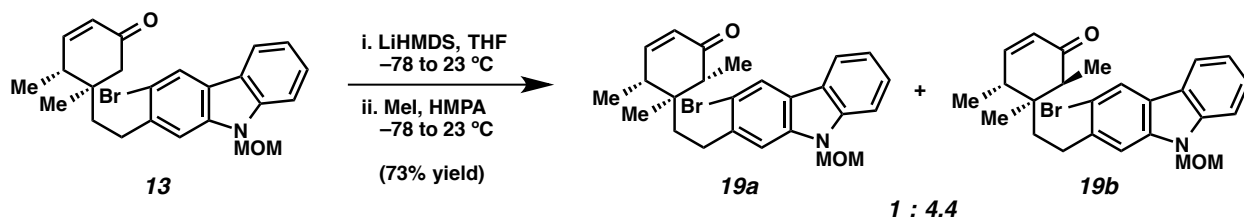
to $-78\text{ }^{\circ}\text{C}$. The solution containing the enolate of **13** was added dropwise to the Eschenmoser's salt suspension over 3 min. The reaction was warmed to room temperature and stirred for 2.5 h. The reaction was quenched with brine (4 mL) and diluted with H_2O (15 mL) and EtOAc (40 mL). The layers were separated and the aqueous layer was extracted with EtOAc (2 x 30 mL). The combined organic layers were dried over MgSO_4 and concentrated under reduced pressure to afford the crude adduct, which was used in the subsequent step without further purification.

The crude adduct was dissolved in CH_2Cl_2 (2.8 mL) and cooled to $0\text{ }^{\circ}\text{C}$. *m*-CPBA (68%, 280.6 mg, 1.11 mmol, 2 equiv) was added and the reaction was stirred for 3 min before warming to room temperature. After an additional 15 min, the reaction was diluted with EtOAc (40 mL) and sat. aq. NaHCO_3 (20 mL). The layers were separated, and the aqueous layer was extracted with EtOAc (2 x 25 mL). The combined organic layers were dried over MgSO_4 and concentrated under reduced pressure to afford the crude product. This compound was further purified by flash chromatography (2.5:1 Hexanes:EtOAc) to provide **16** (190.1 mg, 75% yield, 2 steps) as a white solid. Mp: $143\text{--}144\text{ }^{\circ}\text{C}$; R_f 0.37 (2.5:1 Hexanes:EtOAc); ^1H NMR (500 MHz, CDCl_3): δ 8.17 (s, 1H), 7.97 (app. dt, $J = 7.7, 0.8$, 1H), 7.50 (app. dt, $J = 8.2, 0.8$, 1H), 7.45 (ddd, $J = 8.2, 7.1, 1.1$, 1H), 7.27 (s, 1H), 7.25 (ddd, $J = 7.9, 7.1, 0.9$, 1H) 6.96 (dd, $J = 10.0, 5.8$, 1H), 6.28 (d, $J = 0.9$, 1H), 6.11 (d, $J = 10.0$, 1H), 5.62 (s, 2H), 5.42 (app. t, $J = 1.0$, 1H), 3.27 (s, 3H), 2.83, (app. td, $J = 13.0, 4.8$, 1H), 2.64 (app. td, $J = 12.9, 4.7$, 1H), 2.43 (app. p, $J = 6.7$, 1H), 2.02 (app. td, $J = 13.2, 4.7$, 1H), 1.78 (app. td, $J = 13.2, 4.8$, 1H), 1.35 (s, 3H), 1.07 (d, $J = 7.1$, 3H); ^{13}C NMR (125 MHz, CDCl_3): (24 of 25 C) δ 189.2, 155.2, 148.9, 141.1, 140.2, 139.0, 127.9, 126.5, 124.4, 123.6, 122.4, 121.8, 120.4, 115.3, 110.6, 109.4, 74.3, 56.3, 44.4, 41.7, 40.8, 32.9, 21.3, 15.9; IR (film): 2934, 1668, 1603, 1470, 1452, 1242 cm^{-1} ; HRMS-ESI (m/z) $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{25}\text{H}_{26}\text{BrNO}_2\text{Na}$, 474.1045; found, 474.1042. $[\alpha]_D^{23} +24.9^{\circ}$ ($c = 1.0$, CHCl_3).



Enones 17a and 17b. Compounds **17a** and **17b** were prepared following the general procedure of Lipshutz.⁵ A vial charged with CuCN (35.1 mg, 0.392 mmol, 3.6 equiv) was evacuated, backfilled with N₂ a total of three times, and then taken into the glovebox. Lithium chloride (18.4 mg, 0.434 mmol, 3.9 equiv) was added and the vial was removed from the glovebox. To a separate vial was added prenyl tri(*n*-butyl)stannane (prepared following the procedure of Keck et al.,² 130 μ L, 0.364 mmol, 3.3 equiv). To each vial was added THF (450 μ L) and both were cooled to $-78\text{ }^\circ\text{C}$. Once at $-78\text{ }^\circ\text{C}$, *n*-butyllithium (2.20 M in hexanes, 150 μ L, 0.330 mmol, 3 equiv) was added to the vial containing stannane, causing the solution to turn bright yellow. After 10 min, the yellow lithiate solution was transferred to the vial containing CuCN and the resulting brown mixture was stirred for 10 min. TMSCl (55 μ L, 0.433 mmol, 3.9 equiv) was then added to the brown cuprate solution, followed by enone **16** (49.7 mg, 0.110 mmol, 1 equiv) as a solution in THF (600 μ L) over 2 min. The vial from which the enone solution was taken was then washed with additional THF (300 μ L) and the resulting solution was added to the reaction mixture. After stirring for 1 h, the reaction was quenched with sat. aq. NH₄Cl (700 μ L) and the reaction was warmed to room temperature. The mixture was diluted with H₂O (4 mL) and EtOAc (15 mL). The layers were separated and the aqueous layer extracted with EtOAc (2 x 15 mL). The combined organic layers were dried over MgSO₄ and concentrated under reduced pressure. The crude residue was redissolved in THF (700 μ L) and TBAF (1.0 M in THF, 550 μ L, 0.550 mmol, 5 equiv) was added. After stirring for 5 min, the reaction was diluted with H₂O (8 mL) and EtOAc (15 mL). The layers were separated and the aqueous layer was extracted with EtOAc (2 x 10 mL). The combined organic layers were dried over MgSO₄ and concentrated under reduced pressure to afford a crude mixture of diastereomeric products. These compounds were purified by flash chromatography (4:1 Hexanes:EtOAc) to give a 4.5:1 mixture of homoprenylated diastereomers **17a** and **17b** (39.2 mg, 68% yield) as a colorless oil. Analytical samples of **17a** and **17b** were obtained by preparative thin layer chromatography (3:1

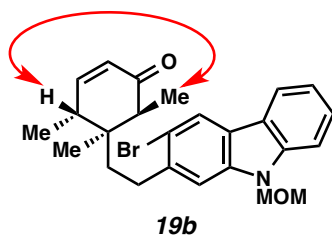
Hexanes:EtOAc). **17a(major diastereomer)**: R_f 0.37 (4:1 Hexanes:EtOAc); $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 8.22 (s, 1H), 8.00 (app. d, $J = 8.0$, 1H), 7.53 (app. d, $J = 8.1$, 1H), 7.48 (ddd, $J = 8.2$, 7.0, 1.2, 1H), 7.35 (s, 1H), 7.28 (app. t, $J = 7.6$, 1H), 6.55 (dd, $J = 10.1$, 2.1, 1H), 6.00 (dd, $J = 10.1$, 3.0, 1H), 5.65 (s, 2H), 5.31 (app. t, $J = 7.4$, 1H), 3.10 (s, 3H), 2.99 (m, 2H), 2.79 (td, $J = 13.1$, 4.6, 1H), 2.48 (d, $J = 9.7$, 1H), 2.39 (m, 1H), 2.10 (m, 1H), 1.84 (m, 2H), 1.75 (m, 1H), 1.74 (s, 3H), 1.69 (s, 3H), 1.53 (m, 1H), 1.19 (d, $J = 7.5$, 3H), 0.74 (s, 3H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3): δ 202.6, 152.5, 141.2, 140.3, 139.2, 132.4, 128.4, 126.6, 124.9, 124.4, 123.7, 122.4, 120.53, 120.51, 115.3, 110.4, 109.4, 74.3, 56.3, 53.9, 44.6, 38.2, 37.9, 31.6, 28.3, 25.9, 23.8, 18.0, 16.3, 15.0; IR (film): 2966, 2929, 1675, 1451, 1241, 1111, 1060 cm^{-1} ; HRMS-ESI (m/z) $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{30}\text{H}_{36}\text{BrNO}_2\text{Na}$, 544.1827; found, 544.1829. $[\alpha]_D^{23} -106.5^\circ$ ($c = 0.2$, CHCl_3). **17b(minor diastereomer)**: R_f 0.30 (4:1 Hexanes:EtOAc); $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 8.22 (s, 1H), 8.00 (app. d, $J = 7.51$, 1H), 7.52 (app. d, $J = 8.2$, 1H), 7.47 (ddd, $J = 8.1$, 7.1, 1.0, 1H), 7.34 (s, 1H), 7.27 (app. t, $J = 7.5$, 1H), 6.49 (app. d, $J = 9.7$, 1H), 5.90 (dd, $J = 10.1$, 2.5, 1H), 5.66 (s, 2H), 5.18 (app. t, $J = 7.2$, 1H), 3.30 (s, 3H), 2.81 (dd, $J = 9.6$, 8.0, 2H), 2.55 (m, 1H), 2.31 (app. d, $J = 9.9$, 1H), 2.03 (m, 2H), 1.85 (m, 2H), 1.76 (m, 1H), 1.71 (s, 3H), 1.65 (s, 3H), 1.53 (m, 1H), 1.08 (d, $J = 7.3$, 3H), 1.07 (s, 3H); $^{13}\text{C NMR}$ (125 MHz, CD_3CN): δ 203.6, 153.6, 142.0, 141.2, 140.3, 132.9, 127.4, 126.6, 125.02, 124.96, 124.2, 123.0, 121.3, 121.2, 115.5, 112.0, 110.7, 74.8, 56.4, 55.8, 42.2, 38.8 (2 carbons by HSQC), 31.4, 26.8, 26.6, 25.8, 19.8, 17.9, 14.0; IR (film): 2963, 2930, 1676, 1451, 1242, 1111 cm^{-1} ; HRMS-ESI (m/z) $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{30}\text{H}_{36}\text{BrNO}_2\text{Na}$, 544.1827; found, 544.1817. $[\alpha]_D^{23} +16.0^\circ$ ($c = 0.1$, CHCl_3).

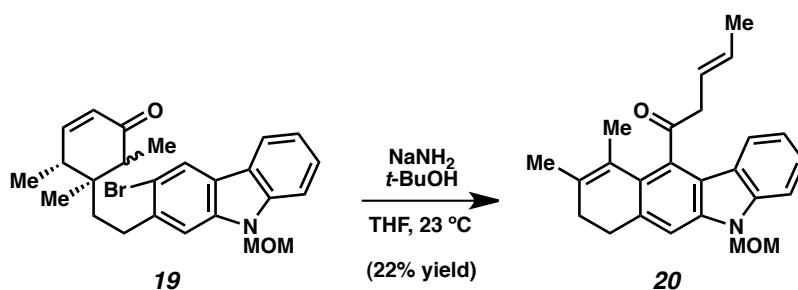


Methylated compounds 19a and 19b. To a solution of LiHMDS (40.3 mg, 0.241 mmol, 1.7 equiv) in THF (500 μL) at $-78 \text{ }^\circ\text{C}$ was added enone **13** (62.7 mg, 0.142 mmol, 1 equiv) as a solution in THF (200 μL). The vial containing the enone solution was then washed with

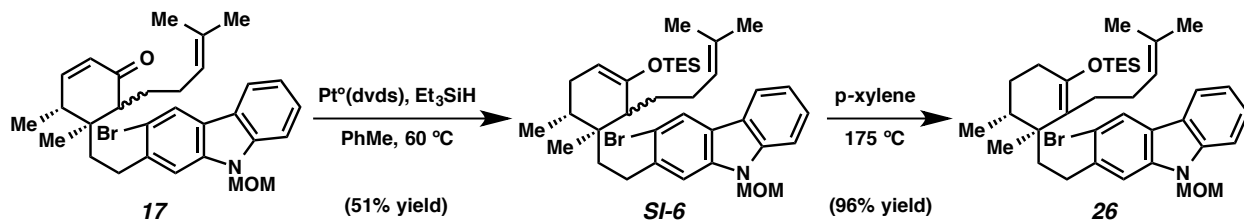
additional THF (200 μ L) and the resulting solution was added to the reaction mixture. The reaction was warmed to room temperature and stirred for 1 h. After recooling to -78 $^{\circ}$ C, MeI (27 μ L, 0.434 mmol, 3.1 equiv) was added, followed by HMPA (100 μ L, 0.575 mmol, 4 equiv). The reaction was immediately allowed to warm to room temperature over 1 h. After 89 h, the reaction was quenched with sat. aq. NH_4Cl (1 mL) and diluted with H_2O (2 mL) and EtOAc (5 mL). The layers were separated, and the aqueous layer extracted with EtOAc (3 x 5 mL). The combined organic layers were dried over MgSO_4 and concentrated under reduced pressure to afford the crude products, which were purified by flash chromatography (3:1 Hexanes:EtOAc), to give **19a** and **19b** (47.4 mg, 73% yield) as a 1 : 4.4 mixture of diastereomers. An analytical sample of the major diastereomer was obtained by preparative thin layer chromatography (3:1 Hexanes:EtOAc). **19b**: R_f 0.21 (3:1 Hexanes:EtOAc); ^1H NMR (500 MHz, CDCl_3): δ 8.21 (s, 1H), 7.99 (d, $J = 7.8$, 1H), 7.52 (d, $J = 8.2$, 1H), 7.47 (ddd, $J = 8.2$, 7.1, 1.2, 1H), 7.34 (s, 1H), 7.27 (ddd, $J = 7.9$, 7.1, 1.1, 1H), 6.61 (dd, $J = 10.1$, 2.4, 1H), 5.93 (dd, $J = 10.1$, 2.3, 1H), 5.66 (s, 2H), 3.29 (s, 3H), 2.87–2.77 (m, 2H), 2.63–2.56 (m, 1H), 2.52 (q, $J = 7.2$, 1H), 1.82–1.69 (m, 2H), 1.20 (d, $J = 7.1$, 3H), 1.12 (d, $J = 7.4$, 3H), 1.10 (s, 3H); ^{13}C NMR (125 MHz, CD_3CN): δ 203.6, 154.1, 142.0, 141.3, 140.4, 127.4, 126.9, 125.0, 124.2, 123.0, 121.3, 121.2, 115.5, 112.1, 110.7, 74.8, 56.4, 49.9, 41.6, 38.0, 37.8, 31.7, 20.5, 13.9, 11.0; IR (film): 2965, 2937, 1676, 1470, 1451, 1242, 1111, 1061 cm^{-1} ; HRMS-ESI (m/z) [$\text{M} + \text{NH}_4$] $^+$ calcd for $\text{C}_{25}\text{H}_{32}\text{BrN}_2\text{O}_2$, 471.16417; found, 471.16228; $[\alpha]_D^{23}$ -12.7° ($c = 0.10$, CHCl_3).

The stereochemistry of the major diastereomer was confirmed by NOESY (500MHz, CDCl_3), as the following interaction was observed:



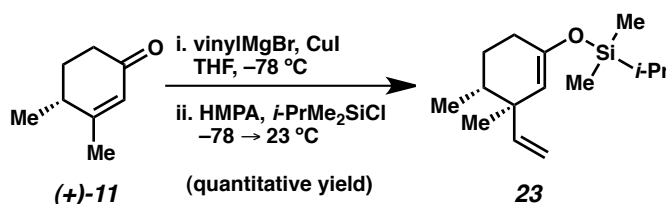


Rearranged product 20. Inside the glovebox, a vial was charged with NaNH_2 (37.9 mg, 0.972 mmol, 11 equiv) and the solid was crushed into a powder. The vial was removed from the glovebox and THF (1.75 mL) was added, followed by *t*-BuOH (31 μL , 0.324 mmol, 3.7 equiv). The vial was placed in a heating block at 40 $^\circ\text{C}$ and stirred for 1 h. After cooling to room temperature under N_2 , enone **19** (40.1 mg, 0.088 mmol, 1 equiv) was added as a solution in THF (1.5 mL). The vial containing **19** was then washed with additional THF (500 μL) and the resulting solution was added to the reaction mixture. The reaction was stirred at room temperature for 3.5 h, then quenched with H_2O (5 mL) and diluted with EtOAc (10 mL). The layers were separated, and the aqueous layer extracted with EtOAc (2 x 10 mL). The combined organic layers were dried over MgSO_4 and concentrated under reduced pressure to afford the crude products. The crude material was further purified by preparative thin layer chromatography (2:1 Hexanes:EtOAc) to afford **20** (7.3 mg, 22% yield) as a light yellow oil. R_f 0.49 (2:1 Hexanes:EtOAc); ^1H NMR (500 MHz, CD_2Cl_2): δ 7.76 (d, $J = 7.6$, 1H), 7.52 (d, $J = 8.0$, 1H), 7.42 (app. t, $J = 7.7$, 1H), 7.37 (s, 1H), 7.16 (app. t, $J = 7.6$, 1H), 5.82–5.73 (m, 1H), 5.66 (s, 2H), 5.62–5.53 (m, 1H), 3.56 (br s, 2H), 3.29 (s, 3H), 2.84 (t, $J = 7.2$, 2H), 2.22 (br s, 2H), 2.01 (s, 3H), 1.97 (s, 3H), 1.71 (dd, $J = 6.3, 1.2$, 3H); ^{13}C NMR (125 MHz, CD_2Cl_2): δ 209.4, 141.3, 139.1, 137.8, 135.4, 131.7, 130.0, 128.3, 126.0, 125.2, 123.4, 122.4, 121.8, 120.4, 117.3, 109.5, 108.8, 74.4, 56.4, 49.1, 31.4, 31.0, 20.8, 18.5, 18.2; IR (film): 2931, 2889, 1699, 1595, 1474, 1332, 1065 cm^{-1} ; HRMS-ESI (m/z) $[\text{M} + \text{NH}_4]^+$ calcd for $\text{C}_{25}\text{H}_{31}\text{N}_2\text{O}_2$, 391.23800; found, 391.23684.



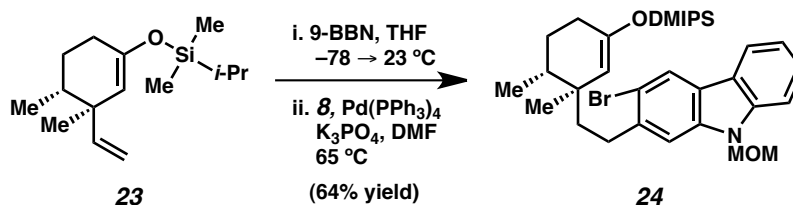
Silyl Enol Ether 26. To a solution of Karstedt's catalyst (~2 wt. % in xylene, 30 μL , 2.6 μmol , 0.1 equiv) at room temperature, was added Et_3SiH (440 μL , 2.75 mmol, 35 equiv) and the mixture was stirred for 10 min. To this mixture was added enone **17** (41.2 mg, 0.079 mmol, 1 equiv) as a solution in toluene (1 mL). The vial from which the enone was taken was washed with additional toluene (600 μL) and the resulting solution was added to the reaction mixture. The reaction was heated to $60\text{ }^\circ\text{C}$ for 2.5 h, then cooled to room temperature and filtered by passage through a pad of celite (95:5 $\text{Et}_2\text{O}:\text{NEt}_3$ eluent). Concentration under reduced pressure afforded the crude silyl enol ether product, which was further purified by flash chromatography (10:1 Hexanes: EtOAc w/ 2% NEt_3) to give the less-substituted silyl enol ether **SI-6** (25.5 mg, 51% yield), which was used for the subsequent isomerization.

Silyl enol ether **SI-6** (11.5 mg, 0.018 mmol) was transferred to a flame-dried Schlenk vessel using 3 portions of anhydrous $p\text{-xylene}$ (1.8 mL total, $p\text{-xylene}$ was sparged with N_2 for ~15 min before use). The Schlenk vessel was sealed under N_2 and placed in an oil bath maintained at $175\text{ }^\circ\text{C}$. After 23 h, the reaction was cooled to room temperature and concentrated under reduced pressure to afford the crude product, which was further purified by flash chromatography (10:1 Hexanes: EtOAc w/ 2% NEt_3) to give **26** (11.0 mg, 96% yield) as a colorless oil. Spectral data matches that reported on page S20.



Silyl Enol Ether 23. To a flask charged with CuI (1.53 g, 8.052 mmol, 2 equiv) was added THF (50 mL). The mixture was cooled to $-78\text{ }^\circ\text{C}$ and vinyl magnesium bromide (1.0 M, 16.1 mL, 16.10 mmol, 4 equiv) was added dropwise over ten min. The reaction was warmed to $-10\text{ }^\circ\text{C}$ for

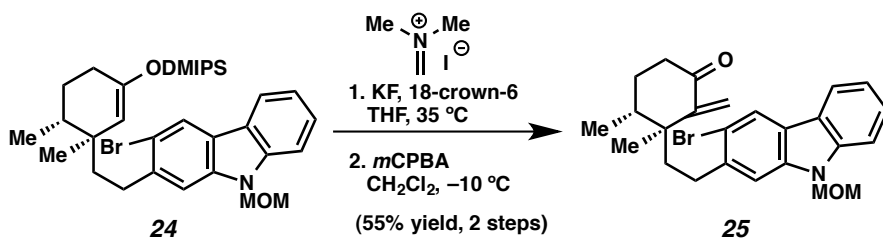
25 min, then recooled to $-78\text{ }^{\circ}\text{C}$. Enone (**+**)-**11** (500 mg, 4.03 mmol, 1 equiv) was then added dropwise as a solution in THF (11 mL) over 15 min. HMPA (11.2 mL, 64.42 mmol, 16 equiv) and DMIPSCI (1.33 mL, 8.46 mmol, 2.1 equiv) were then added to the reaction mixture as a solution in THF (6 mL). The reaction was then allowed to warm to room temperature and was stirred for 12 h. The reaction was recooled to $0\text{ }^{\circ}\text{C}$ and quenched with NEt_3 (10 mL). The mixture was allowed to stir for 1 h and then diluted with H_2O (30 mL) and Et_2O (30 mL). The layers were separated and the aqueous layer was filtered over celite, which was washed with Et_2O (300 mL). The organic layer was washed with brine (30 mL) and the aqueous layer was back-extracted with Et_2O (2 x 20 mL). The combined organic layers were dried over MgSO_4 and concentrated under reduced pressure. The crude product was purified via flash chromatography (19:1 Hexanes: NEt_3) to afford **23** (1.01 g, quantitative yield) as a yellow oil. R_f 0.30 (Hexanes); $^1\text{H NMR}$ (300 MHz, C_6D_6): δ 5.80 (dd, $J = 17.4, 10.5, 1\text{H}$), 5.05 (dd, $J = 17.4, 1.5, 1\text{H}$), 5.00 (dd, $J = 10.5, 1.5, 1\text{H}$), 4.75 (s, 1H), 1.92–2.14 (m, 2H), 1.31–1.56 (m, 4H), 1.01 (d, $J = 6.5, 6\text{H}$), 0.97 (s, 3H), 0.81 (d, $J = 6.4, 3\text{H}$), 0.14 (s, 6H); $^{13}\text{C NMR}$ (125 MHz, C_6D_6): δ 151.0, 149.7, 112.9, 112.3, 42.2, 37.4, 30.2, 27.8, 21.7, 17.5, 16.1, 15.8, $-2.79, -2.82$; IR (film): 2958, 2927, 2866, 1663, 1463, 1370, 1189 cm^{-1} ; HRMS-ESI (m/z) [$\text{M} + \text{H}$] $^+$ calcd for $\text{C}_{15}\text{H}_{29}\text{OSi}$, 253.1988; found, 253.1987. $[\alpha]_D^{23} -8.0^{\circ}$ ($c = 0.1, \text{EtOAc}$).



Coupled Silyl Enol Ether 24. A vial charged with silyl enol ether **23** (552.2 mg, 2.19 mmol, 2 equiv) was cooled to $-78\text{ }^{\circ}\text{C}$. 9-BBN (0.5 M in THF, 5.3 mL, 2.65 mmol, 2.4 equiv) was then added dropwise over 5 min. The reaction was allowed to warm to room temperature and stirred for 5 h. To a separate vial was added $\text{Pd}(\text{PPh}_3)_4$ (252.8 mg, 0.219 mmol, 0.2 equiv) in the glovebox. The vial was removed, DMF (4.5 mL) was added, and the solution was sparged with N_2 for 10 min. K_3PO_4 (349.3 mg, 1.65 mmol, 1.5) and carbazole **8** (480.6 mg, 1.10 mmol, 1 equiv) were added to the DMF solution. The THF solution was then added to the DMF mixture

and the reaction was heated to 65 °C for 24 h. The reaction was then allowed to cool to room temperature, quenched with NEt_3 (2.5 mL), and diluted with H_2O (20 mL) and EtOAc (30 mL). The layers were separated and the aqueous layer was extracted with EtOAc (2 x 30 mL). The combined organic layers were washed with brine (25 mL), dried over Na_2SO_4 , and concentrated under reduced pressure. The compound was purified by flash chromatography (20:2:1 Hexanes:Acetone: NEt_3) to afford **24** (379.6 mg, 64% yield) as a yellow oil. R_f 0.45 (20:2:1 Hexanes:Acetone: NEt_3); ^1H NMR (300 MHz, CD_3CN): δ 8.26 (s, 1H), 8.03 (d, $J = 7.7$, 1H), 7.58 (d, $J = 8.6$, 1H), 7.50 (s, 1H), 7.46 (ddd, $J = 8.4, 7.2, 1.2$, 1H), 7.24 (ddd, $J = 8.0, 7.2, 1.0$, 1H), 5.64 (s, 2H), 4.81 (d, $J = 1.7$, 1H), 3.23 (s, 3H), 2.80 (m, 2H), 2.04–2.08 (m, 1H), 1.68–1.80 (m, 3H), 1.45–1.60 (m, 4H), 0.99 (m, 6H), 0.92 (d, $J = 6.9$, 3H), 0.88 (s, 3H), 0.17 (s, 6H); ^{13}C NMR (125 MHz, C_6D_6): δ 150.7, 141.5, 140.7, 140.6, 126.5, 124.8, 123.9, 122.9, 120.8, 120.6, 115.9, 114.1, 111.0, 109.6, 74.0, 55.5, 43.0, 38.2, 34.0, 33.2, 30.4, 28.0, 23.6, 17.14, 17.13, 15.7, 15.4, –3.11, –3.14; IR (film): 2925, 2864, 1665, 1450, 1241, 1111, 1067 cm^{-1} ; HRMS-ESI (m/z) [$\text{M} + \text{NH}_4$] $^+$ calcd for $\text{C}_{29}\text{H}_{44}\text{BrN}_2\text{O}_2\text{Si}$, 559.23224; found, 559.23499. $[\alpha]_D^{23}$ –12.0° ($c = 0.1$, EtOAc).

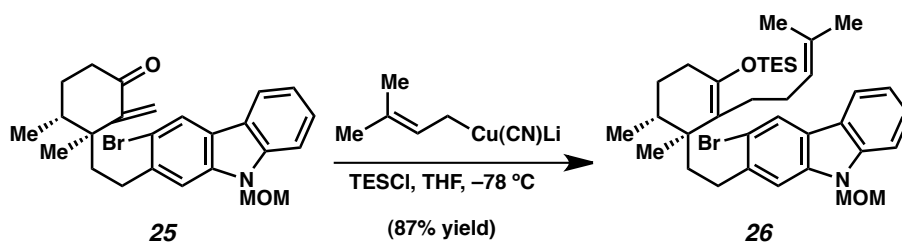
NOTE: The purification reported above typically gave compound **24** with a purity of ~70–75% according to ^1H -NMR analysis with an external standard, despite ^1H -NMR not showing impurities. Nonetheless, this material was used in the subsequent step without further purification.



Enone 25. To a vial inside the glovebox containing silyl enol ether **24** (63.7 mg, 0.117 mmol, 1 equiv) were added 18-crown-6 (123.4 mg, 0.467 mmol, 4 equiv), Eschenmoser's salt (215.4 mg, 1.16 mmol, 10 equiv), and KF (27.2 mg, 0.468 mmol, 4 equiv). The vial was removed from the glovebox, THF (1.3 mL) was added, and the mixture was warmed to 35 °C for 14 h. The reaction was then cooled to room temperature and diluted with EtOAc (10 mL), brine (5 mL),

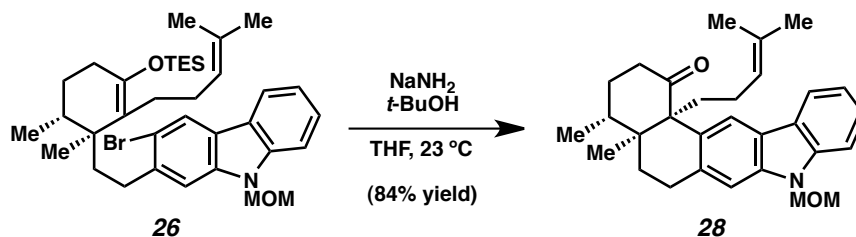
and H₂O (5 mL). The layers were separated, and the aqueous layer was extracted with EtOAc (3 x 10 mL). The combined organic layers were dried over Na₂SO₄ and concentrated under reduced pressure to afford the crude adduct, which was used without further purification.

The crude adduct was dissolved in CH₂Cl₂ (2.0 mL) and cooled to –10 °C. *m*-CPBA (75%, 52.2 mg, 0.233 mmol, 2 equiv) was added and the reaction was stirred for 30 min at –10 °C. The reaction was diluted with sat. aq. NaHCO₃ (5 mL) and EtOAc (10 mL). The layers were separated, and the aqueous layer was extracted with EtOAc (2 x 15 mL). The combined organic layers were dried over Na₂SO₄ and concentrated under reduced pressure to afford the crude product. Purification by flash chromatography (5:1 Hexanes:EtOAc) provided **25** (29.2 mg, 55% yield, 2 steps) as a colorless oil. R_f 0.14 (5:1 Hexanes:EtOAc); ¹H NMR (500 MHz, CD₃CN): δ 8.28 (s, 1H), 8.06 (app. dt, *J* = 7.6, 1.0, 1H), 7.60 (app. d, *J* = 8.3, 1H), 7.51 (s, 1H), 7.48 (ddd, *J* = 8.3, 7.1, 1.2, 1H), 7.26 (ddd, *J* = 7.9, 7.2, 0.9, 1H) 5.83 (d, *J* = 1.4, 1H), 5.68 (s, 2H), 5.33 (d, *J* = 1.3, 1H), 3.24 (s, 3H), 2.83 (m, 2H), 2.51 (ddd, *J* = 17.3, 9.0, 7.0, 1H), 2.39, (app. dt, *J* = 17.2, 6.1, 1H), 2.18 (m, 1H), 2.05 (m, 1H), 1.77 (m, 3H), 1.18 (s, 3H), 1.09 (d, *J* = 7.0, 3H); ¹³C NMR (125 MHz, CD₃CN): δ 203.7, 154.4, 142.0, 141.3, 140.2, 127.4, 125.0, 124.1, 123.0, 121.3, 121.2, 119.0, 115.5, 112.0, 110.7, 74.8, 56.4, 45.0, 41.3, 37.7, 35.9, 32.2, 27.2, 22.5, 15.6; IR (film): 2938, 1691, 1603, 1470, 1452, 1242, 1112 cm⁻¹; HRMS-ESI (*m/z*) [M + NH₄]⁺ calcd for C₂₅H₃₂BrN₂O₂, 471.1635; found, 471.1642. [α]_D²³ +28.0° (*c* = 0.1, EtOAc).

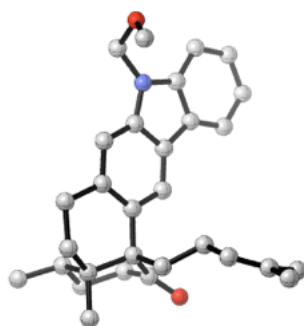
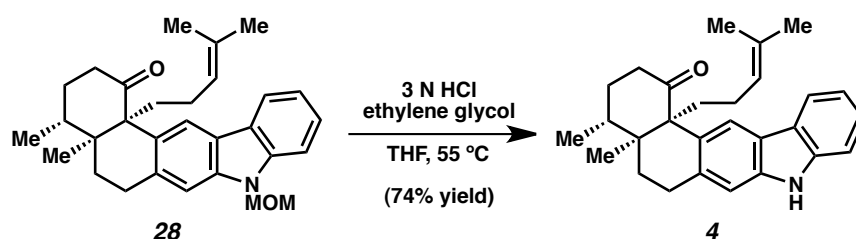


Silyl Enol Ether 26. Compound **26** was prepared following the general procedure of Lipshutz.⁵ A vial was charged with CuCN (36.7 mg, 0.410 mmol, 3.5 equiv) and lithium chloride (18.4 mg, 0.433 mmol, 3.7 equiv) inside a glovebox and then the vial was removed from the glovebox. To this vial was added THF (0.5 mL) and the mixture was allowed to stir at 23 °C for 5 min, until the solids fully dissolved. The pale green solution was then cooled to –78 °C. To a separate vial

was added prenyl tri(*n*-butyl)stannane (prepared following the procedure of Keck et al.,² 133.6 μ L, 0.374 mmol, 3.2 equiv). To the stannane was added THF (0.5 mL) and the solution immediately cooled to -78 °C. Once at -78 °C, *n*-butyllithium (2.40 M in hexanes, 141.3 μ L, 0.339 mmol, 2.9 equiv) was added to the vial containing stannane, causing the solution to turn bright yellow. After 30 min, the yellow lithiate solution was transferred to the vial containing CuCN via chilled cannulation. To the resulting brown mixture was added TESCl (72.7 μ L, 0.433 mmol, 3.7 equiv) and the solution was allowed to stir cold. After 20 min, enone **25** (53.0 mg, 0.117 mmol, 1 equiv) as a solution in THF (1.0 mL) was added slowly via syringe. The vial from which the enone solution was taken was then washed with additional THF (0.2 mL) and the resulting solution was added to the reaction mixture. After stirring for 1 h, the reaction was quenched with triethylamine (0.5 mL) and sat. aq. NaHCO₃ (1 mL), and then warmed to room temperature. The mixture was diluted with H₂O (5 mL) and EtOAc (6 mL). The layers were separated and the aqueous layer was extracted with EtOAc (4 x 6 mL). The combined organic layers were dried over Na₂SO₄ and concentrated under reduced pressure to deliver the crude product. Purification by flash chromatography (10:1 Hexanes:EtOAc, 2% Et₃N) gave **26** (64.9 mg, 87% yield) as a colorless oil. R_f 0.77 (3:1 Hexanes:EtOAc); ¹H NMR (500 MHz, CD₂Cl₂): δ 8.22 (s, 1H), 8.01 (app. d, $J = 7.6$, 1H), 7.54 (app. d, $J = 8.1$, 1H), 7.47 (ddd, $J = 8.2, 7.1, 1.1$, 1H), 7.39 (s, 1H), 7.27 (app. t, $J = 7.6$, 1H), 5.65 (s, 2H), 5.19 (app. t, $J = 7.0$, 1H), 3.29 (s, 3H), 2.84 (td, $J = 13.1, 4.8$, 1H), 2.56 (td, $J = 13.1, 4.6$, 1H), 2.34 (m, 2H), 2.24 (m, 1H), 2.06 (m, 2H), 1.86 (m, 3H), 1.73 (m, 2H), 1.69 (s, 3H), 1.66 (m, 1H), 1.61 (s, 3H), 1.03 (t, $J = 7.8, 9H$), 0.98 (d, $J = 6.8, 3H$), 0.95 (s, 3H), 0.72 (q, $J = 7.8, 6H$); ¹³C NMR (125 MHz, CD₂Cl₂): δ 146.7, 141.4, 140.8, 140.7, 131.0, 126.7, 126.0, 124.3, 123.5, 122.7, 121.5, 120.6, 120.58, 115.7, 110.7, 109.8, 74.6, 56.4, 41.5, 39.1, 34.0, 32.7, 30.7, 28.7, 27.6, 27.5, 25.8, 21.8, 17.9, 16.5, 7.1, 6.2; IR (film): 2956, 1711, 1657, 1603, 1451, 1241 cm⁻¹; HRMS-ESI (m/z) [M + H]⁺ calcd for C₃₆H₅₃BrNO₂Si, 638.3023; found, 638.3044. $[\alpha]_D^{23} -56.0^\circ$ ($c = 0.1$, EtOAc).

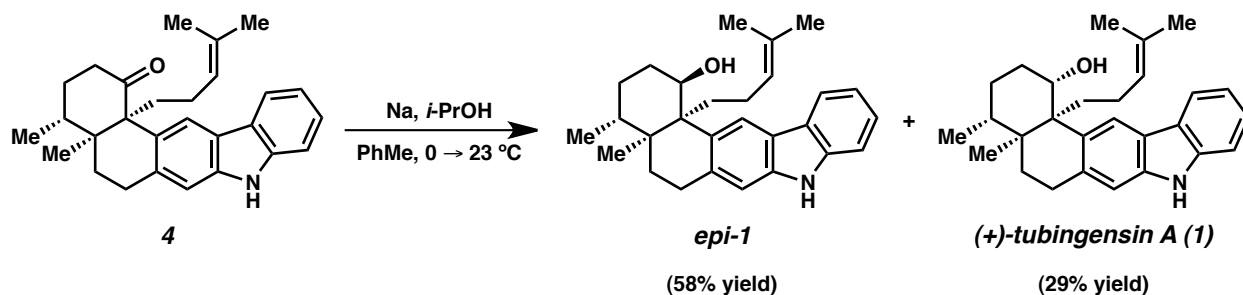


Decalin 28. To a 20-mL vial inside the glovebox was added NaNH_2 (41.5 mg, 1.064 mmol, 11 equiv) and the solid was crushed into a powder. The vial was removed from the glovebox and THF (2.0 mL) was added, followed by $t\text{-BuOH}$ (29.6 μL , 0.309 mmol, 3.2 equiv). The vial was placed in a heating block at 40 °C and stirred for 1 h. After cooling to room temperature under N_2 , silyl enol ether **26** (61.8 mg, 0.097 mmol, 1 equiv) was added as a solution in THF (1.0 mL). The vial containing **26** was then washed with additional THF (1.0 mL) and the resulting solution was added to the reaction mixture. The reaction was stirred at 23 °C for 3 h, quenched with H_2O (3 mL), and then diluted with EtOAc (10 mL) and sat. aq. NH_4Cl (4 mL). The layers were separated, and the aqueous layer extracted with EtOAc (3 x 8 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure to afford the crude product. Purification by flash chromatography (8:1 Hexanes:EtOAc) gave **28** (36.0 mg, 84% yield) as a white solid. Crystals suitable for X-ray diffraction studies (CCDC 984476) were obtained using a sample of racemic **28** by vapor diffusion ($\text{CHCl}_3/\text{Heptanes}$). Mp: 177 °C (*rac.*); R_f 0.39 (8:1 Hexanes:EtOAc); ^1H NMR (500 MHz, CDCl_3): δ 7.96 (d, $J = 7.7$, 1H), 7.49 (d, $J = 8.1$, 1H), 7.43 (ddd, $J = 8.2$, 7.1, 1.1, 1H), 7.31 (s, 2H), 7.23 (ddd, $J = 7.9$, 7.0, 1.0, 1H), 5.66–5.61 (m, 2H), 4.96 (app. dt, $J = 7.1$, 1.4, 1H), 3.34 (s, 3H), 3.17–3.02 (m, 2H), 2.87–2.78 (m, 1H), 2.26 (dt, $J = 12.8$, 3.3, 1H), 2.22–1.99 (m, 4H), 1.76 (ddd, $J = 14.5$, 7.1, 1.3, 1H), 1.70–1.63 (m, 2H), 1.56 (s, 3H), 1.45 (s, 3H), 1.44–1.36 (m, 1H), 1.21–1.11 (m, 1H), 0.91 (d, $J = 6.8$, 3H), 0.85 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3): δ 215.7, 141.2, 139.7, 133.9, 131.5, 129.7, 126.0, 125.2, 123.6, 121.9, 121.8, 120.4, 120.1, 109.4, 109.1, 74.4, 61.4, 56.4, 43.8, 39.7, 33.5, 32.2, 32.1, 28.5, 26.3, 25.8, 25.4, 17.8, 16.2, 15.8; IR (film): 2959, 2928, 1697, 1474, 1241 cm^{-1} ; HRMS-ESI (m/z) [$\text{M} + \text{H}$] $^+$ calcd for $\text{C}_{30}\text{H}_{38}\text{NO}_2$, 444.28971; found, 444.28781. $[\alpha]_D^{23} +80.0^\circ$ ($c = 0.10$, CHCl_3).

X-ray structure of **28**

Ketone 4. To a solution of **28** (11.2 mg, 0.025 mmol, 1 equiv) in THF (2 mL) was added ethylene glycol (100 μ L, 1.79 mmol, 72 equiv) and 3 N HCl (250 μ L, 0.750 mmol, 30 equiv). The reaction was capped and heated to 55 $^{\circ}$ C. After 20.5 h the reaction was cooled to room temperature and diluted with Et₂O (20 mL) and sat. aq. NaHCO₃ (5 mL). The layers were separated, and the aqueous layer was extracted with Et₂O (2 x 15 mL). The combined organic layers were dried over MgSO₄ and concentrated under reduced pressure to provide the crude product. Purification by flash chromatography (5:1 Hexanes:EtOAc) provided **4** (7.5 mg, 74% yield) as an amorphous white solid. *R*_f 0.66 (Benzene eluent); ¹H NMR (500 MHz, CDCl₃): δ 7.96 (d, *J* = 8.1, 1H), 7.88 (s, 1H), 7.39–7.35 (m, 2H), 7.30 (s, 1H), 7.21–7.17 (m, 2H), 5.00–4.94 (m, 1H), 3.14–2.98 (m, 2H), 2.90–2.80 (m, 1H) 2.26 (dt, *J* = 12.9, 3.2, 1H), 2.22–1.98 (m, 4H), 1.77–1.71 (m, 1H), 1.70–1.62 (m, 2H), 1.57 (s, 3H), 1.45 (s, 3H), 1.43–1.37 (m, 1H), 1.21–1.11 (m, 1H), 0.90 (d, *J* = 6.8, 3H), 0.85 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 215.8, 140.0, 138.7, 133.6, 131.4, 129.1, 125.8, 125.2, 123.5, 121.9, 121.7, 120.4, 119.5, 110.60, 110.57, 61.4, 43.7, 39.7, 33.5, 32.2, 32.1, 28.5, 26.2, 25.8, 25.4, 17.8, 16.2, 15.8 IR (film): 3411, 2960, 2928,

1689, 1466, 1243 cm^{-1} ; HRMS-ESI (m/z) [$M + H$] $^+$ calcd for $\text{C}_{28}\text{H}_{34}\text{NO}$, 400.26349; found, 400.26270; $[\alpha]_D^{23} +104.7^\circ$ ($c = 0.10$, CHCl_3).



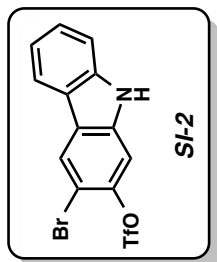
Tubingensin A (1) and epi-Tubingensin A (epi-1). To a solution of ketone **4** (5.7 mg, 0.014 mmol, 1 equiv) in toluene (950 μL) was added $i\text{-PrOH}$ (90 μL , 1.18 mmol, 84 equiv), and the reaction was cooled to 0 $^\circ\text{C}$. Sodium metal (11.1 mg, 0.483 mmol, 35 equiv), after being briefly immersed in hexanes to remove any mineral oil, was added to the reaction. After 2 h the reaction was warmed to room temperature and stirred for an additional 1 h. The reaction was quenched with sat. aq. NH_4Cl (2 mL) and diluted with H_2O (2 mL) and Et_2O (10 mL). The layers were separated, and the aqueous layer was extracted with Et_2O (2 x 10 mL). The combined organic layers were dried over MgSO_4 . Evaporation of the solvent under reduced pressure afforded the crude products, which were purified by preparative thin layer chromatography (8:1:1 Hexanes: CH_2Cl_2 :Acetone) to afford **1** (1.7 mg, 29% yield) and **epi-1** (3.3 mg, 58% yield) as colorless oils. **Tubingensin A (1)**: R_f 0.55 (benzene eluent); $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 8.00 (d, $J = 7.8$, 1H), 7.94 (s, 1H), 7.81 (s, 1H), 7.39–7.44 (m, 2H), 7.19 (ddd, $J = 7.7, 5.8, 1.8$, 1H), 7.14 (s, 1H), 5.03 (app. t, $J = 6.9$, 1H), 4.98 (s, 1H), 3.07–2.98 (m, 1H), 2.90 (dd, $J = 17.5, 6.7$, 1H), 2.13–1.97 (m, 3H), 1.84–1.65 (m, 5H), 1.60 (s, 3H), 1.59–1.50 (m, 3H), 1.44 (s, 3H), 1.23 (s, 3H), 1.20–1.16 (m, 1H), 0.86 (d, $J = 5.9$, 3H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3): δ 140.1, 138.0, 135.3, 132.6, 131.7, 125.5, 125.2, 123.9, 121.5, 119.9, 119.3, 118.6, 110.8, 110.6, 71.5, 47.4, 38.9, 35.0, 32.7, 29.7, 29.5, 27.2, 25.8, 25.5, 23.2, 18.5, 17.8, 16.4; IR (film): 3413, 2928, 1612, 1467, 1242 cm^{-1} ; HRMS-ESI (m/z) [$M - H$] $^-$ calcd for $\text{C}_{28}\text{H}_{34}\text{NO}$, 400.26349; found, 400.26387; $[\alpha]_D^{23} +14.0^\circ$ ($c = 0.10$, CHCl_3). **epi-Tubingensin A (epi-1)**: R_f 0.55 (benzene eluent); $^1\text{H NMR}$ (500 MHz, C_6D_6): δ 9.43 (s, 1H), 8.13 (d, $J = 7.8$, 1H), 7.32 (ddd, $J = 8.2, 7.0,$

1.1, 1H), 7.13 (ddd, $J = 8.0, 7.0, 1.0$, 1H), 7.07, (app. dt, $J = 8.1, 0.8$, 1H), 6.86 (s, 1H), 6.54 (s, 1H), 5.2–5.14 (m, 1H), 3.90 (dd, $J = 12.7, 3.7$, 1H), 2.99–2.90 (m, 1H), 2.85 (dd, $J = 17.3, 7.2$, 1H), 2.47–2.38 (m, 1H), 2.17–2.07 (m, 1H), 2.00–1.90 (m, 3H), 1.80–1.66 (m, 2H), 1.60 (s, 3H), 1.56–1.48 (m, 1H), 1.44 (s, 3H), 1.40–1.33 (m, 1H), 1.29–1.17 (m, 3H), 0.89 (s, 3H), 0.73 (d, $J = 6.9$, 3H); ^{13}C NMR (125 MHz, C_6D_6): δ 140.5, 138.5, 135.4, 132.2, 130.4, 126.7, 125.3, 124.9, 123.2, 122.4, 120.7, 119.5, 110.5, 110.1, 77.5, 49.6, 41.0, 39.1, 32.3, 32.2, 30.7, 29.8, 27.8, 27.0, 25.8, 17.8, 16.6, 16.4; IR (film): 3411, 2927, 1612, 1490, 1465, 1242; HRMS-ESI (m/z) $[\text{M} - \text{H}]^-$ calcd for $\text{C}_{28}\text{H}_{34}\text{NO}$, 400.26349; found, 400.26470; $[\alpha]_D^{23} +24.7^\circ$ ($c = 0.10$, CHCl_3).

^1H NMR and ^{13}C NMR Spectra:

AEG-5-35b3

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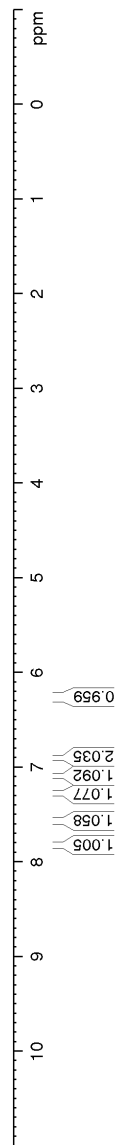
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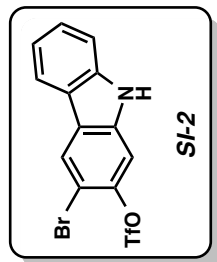
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105.29
105.25



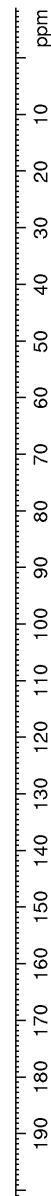
Current Data Parameters
 NAME AEG-5-35bC6D6C13
 EXPNO 2
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20121205
 Time_ 8.56
 INSTRUM av500
 PROBHD 5 mm DCH 13C-1
 PULPROG zgpg30
 TD 65536
 SOLVENT C6D6
 NS 143
 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
 P.CPD2 80.00 usec
 PLW2 13.50000000 W
 PLW12 0.21094000 W
 PLW13 0.13500001 W

F2 - Processing parameters
 SI 131072
 SF 125.7577432 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40



AEG-5-36a

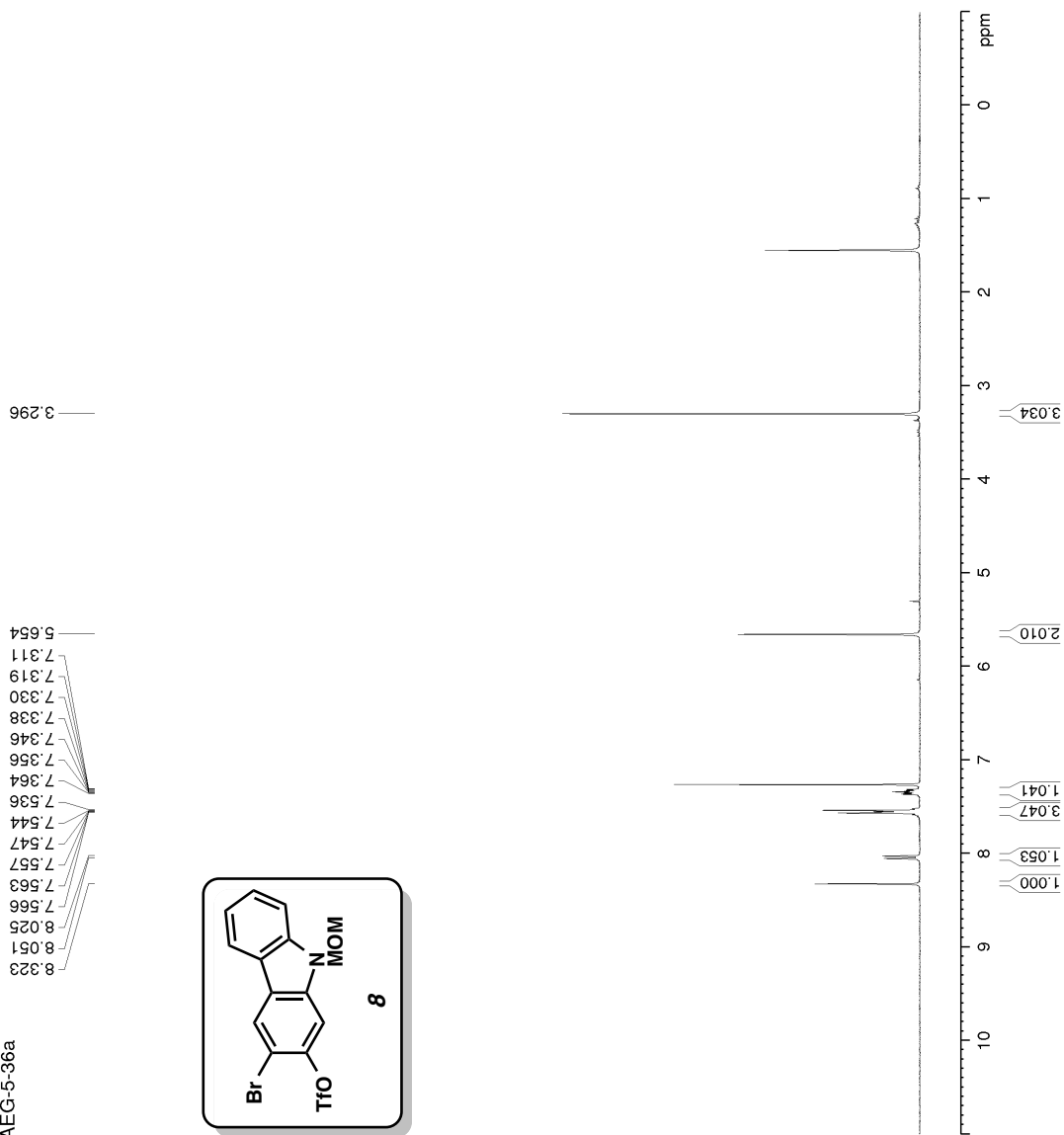
Current Data Parameters
 NAME AEG-5-36a
 EXPNO 1
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20121128
 Time 18.34
 INSTRUM av300
 PROBHD 5 mm PABBO BB-
 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 16
 DS 0
 SWH 5995.204 Hz
 FIDRES 0.091480 Hz
 AQ 5.4657025 sec
 RG 812.7
 DW 83.400 usec
 DE 6.00 usec
 TE 297.7 K
 D1 2.00000000 sec
 TD0 1

===== CHANNEL f1 =====

NUC1 1H
 P1 12.00 usec
 PL1 -2.00 dB
 PL1W 14.76977634 W
 SFO1 300.1318008 MHz

F2 - Processing parameters
 SI 65536
 SF 300.1300121 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.40



AEG-5-36aC13

```

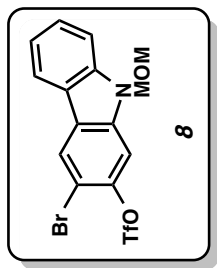
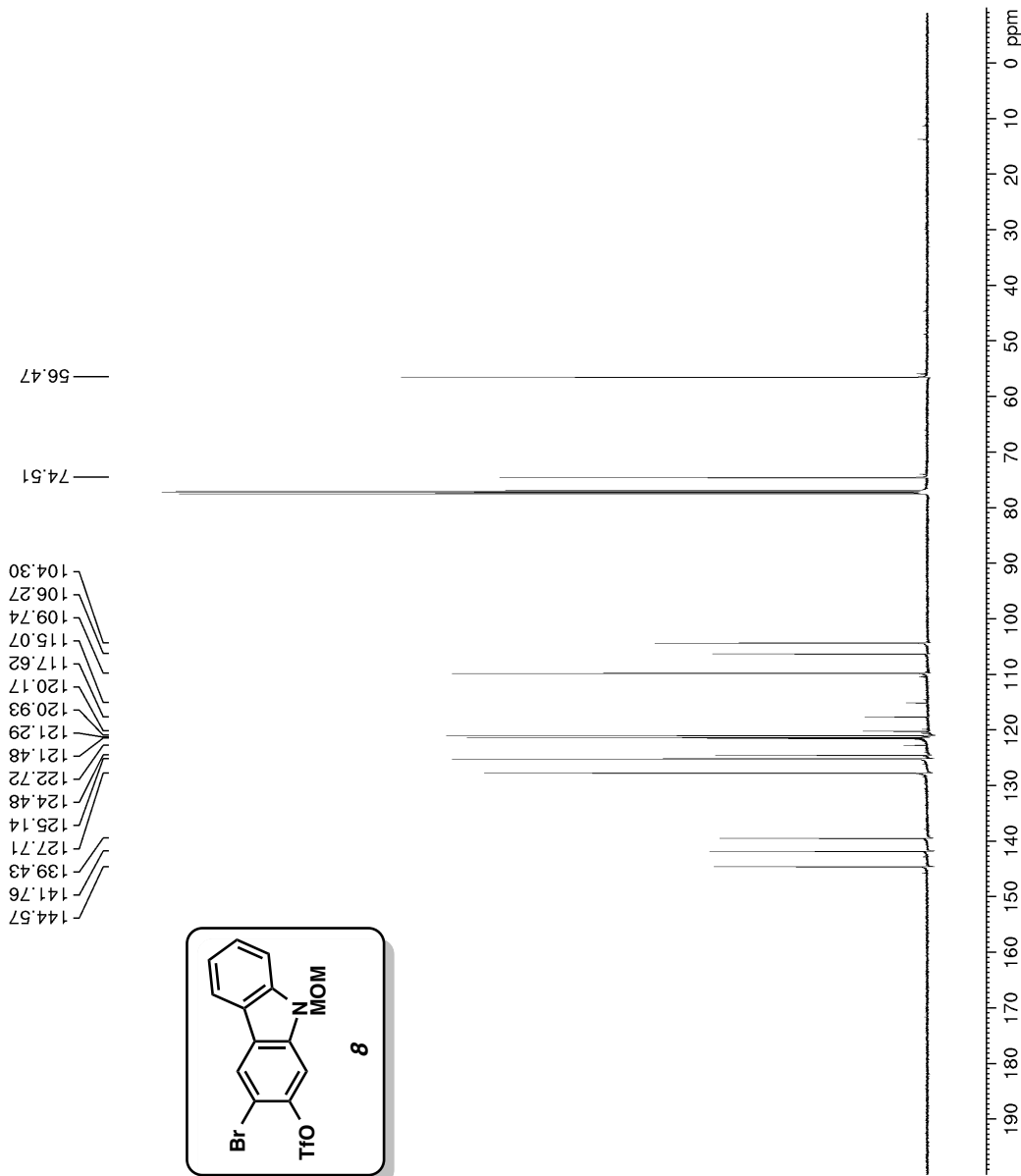
Current Data Parameters
NAME   AEG-5-36aC13
EXPNO   2
PROCNO   1

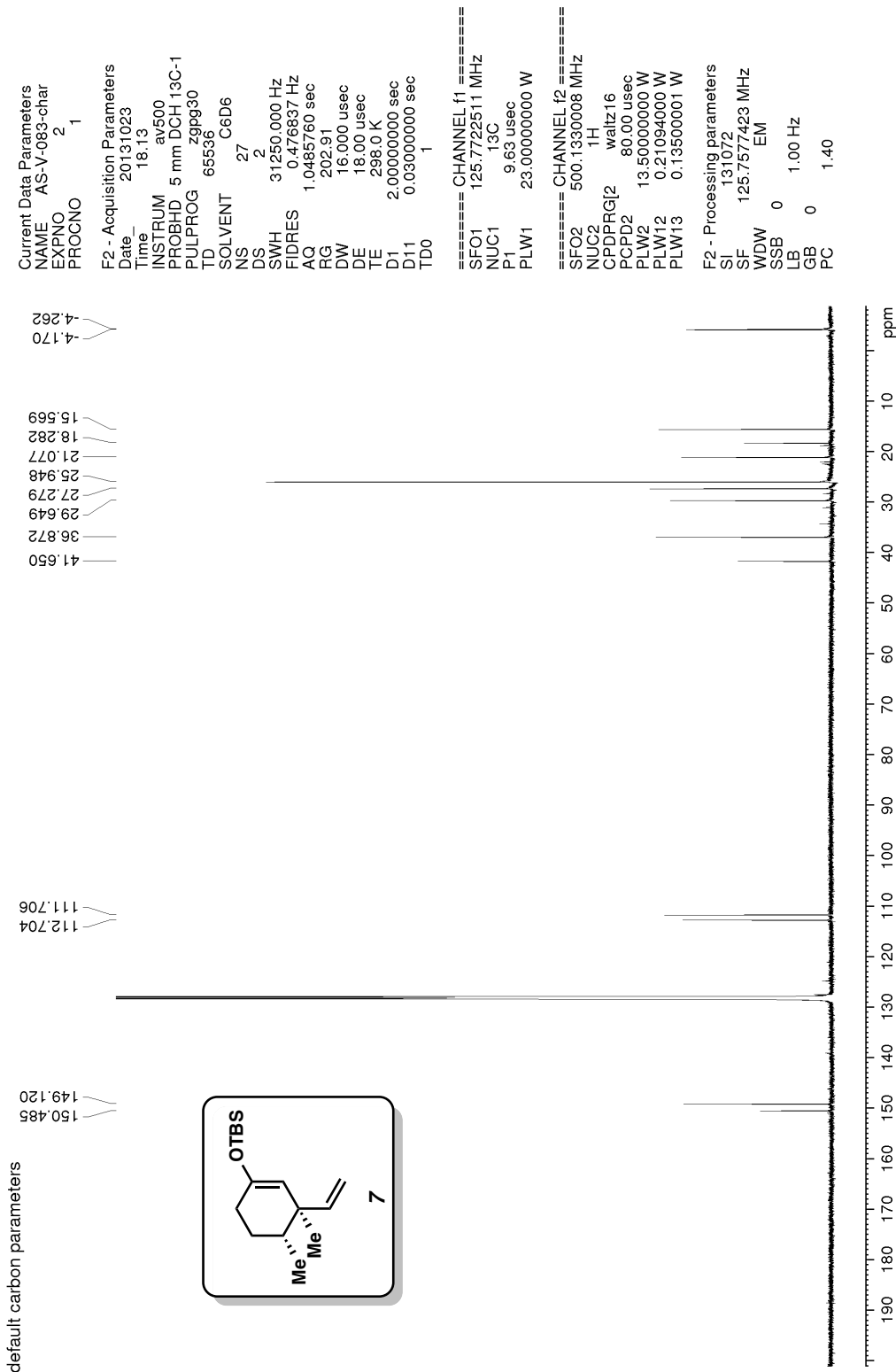
F2 - Acquisition Parameters
Date_   20121218
Time    11.43
INSTRUM av500
PROBHD  5 mm DCH 13C-1
PULPROG zgpg30
TD      65536
SOLVENT CDCI3
NS      32
DS      2
SWH     31250.000 Hz
FIDRES  0.476837 Hz
AQ      1.0485760 sec
RG      202.91
DW      16.000 usec
DE      18.00 usec
TE      298.0 K
D1      2.00000000 sec
D11     0.03000000 sec
TD0     1

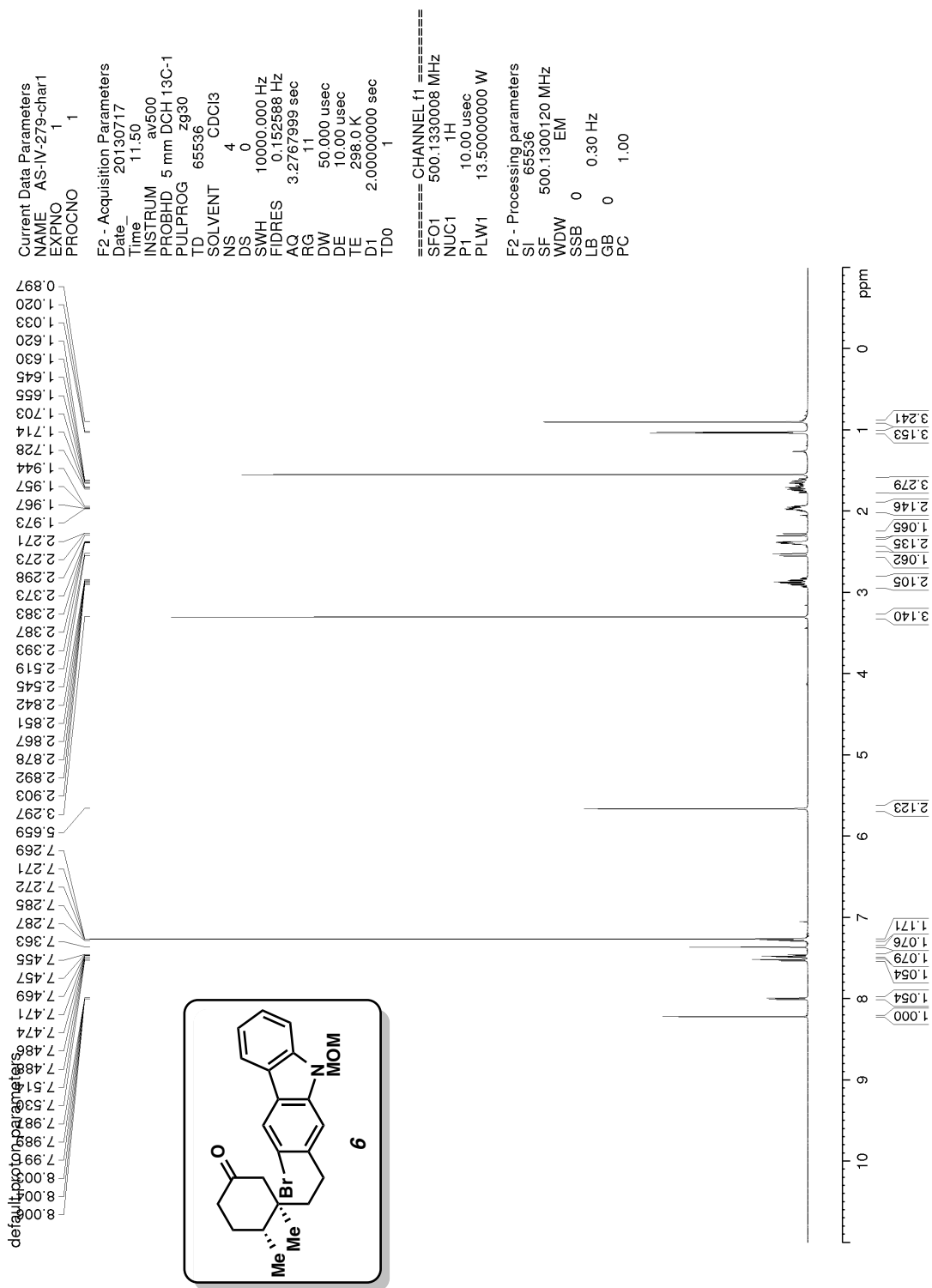
===== CHANNEL f1 =====
SFO1    125.7722511 MHz
NUC1    13C
P1      9.63 usec
PLW1    23.00000000 W

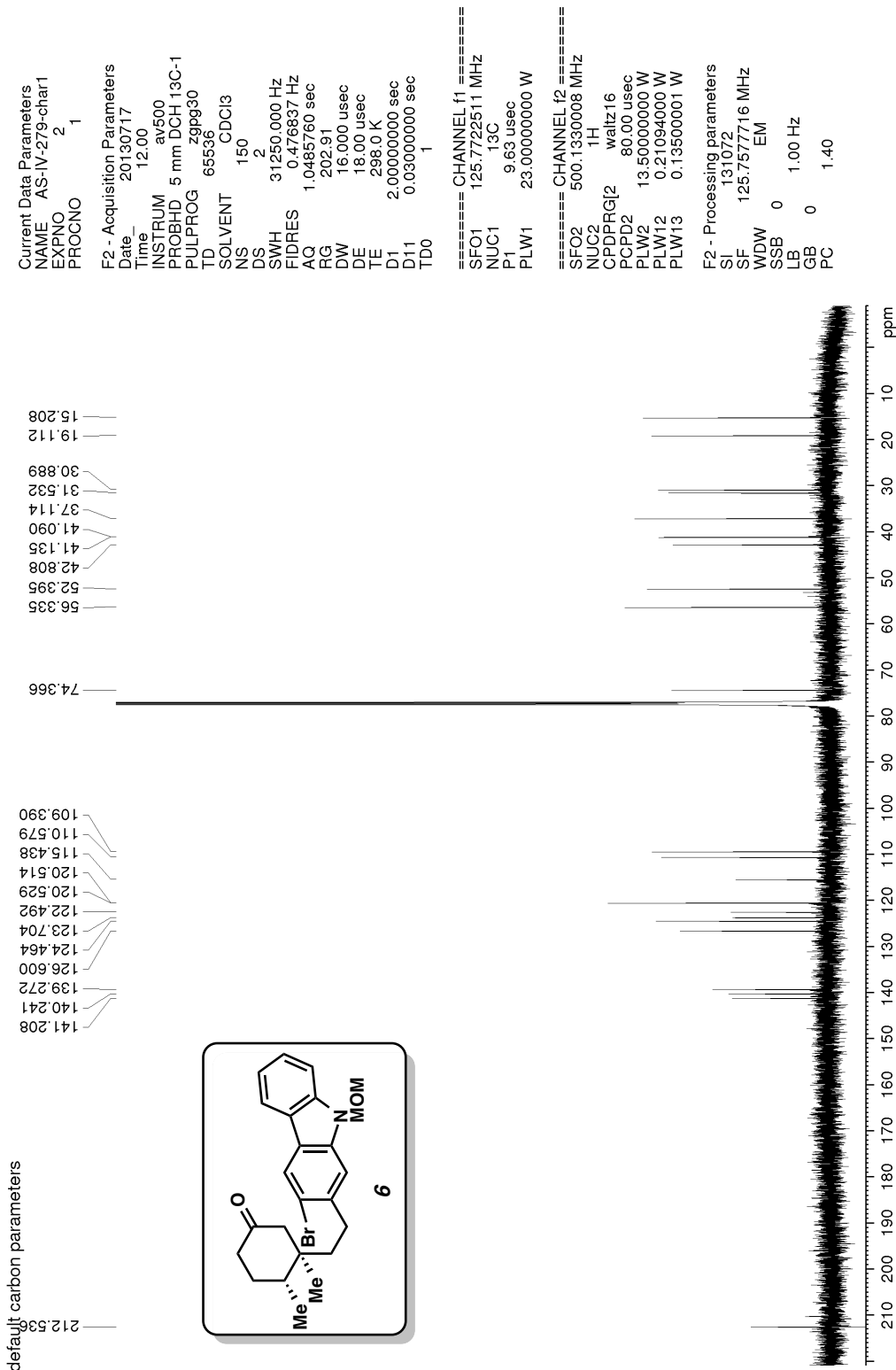
===== CHANNEL f2 =====
SFO2    500.1330008 MHz
NUC2    1H
CPDPRG2 waltz16
PCPD2   80.00 usec
PLW2    13.50000000 W
PLW12   0.21094000 W
PLW13   0.13500001 W

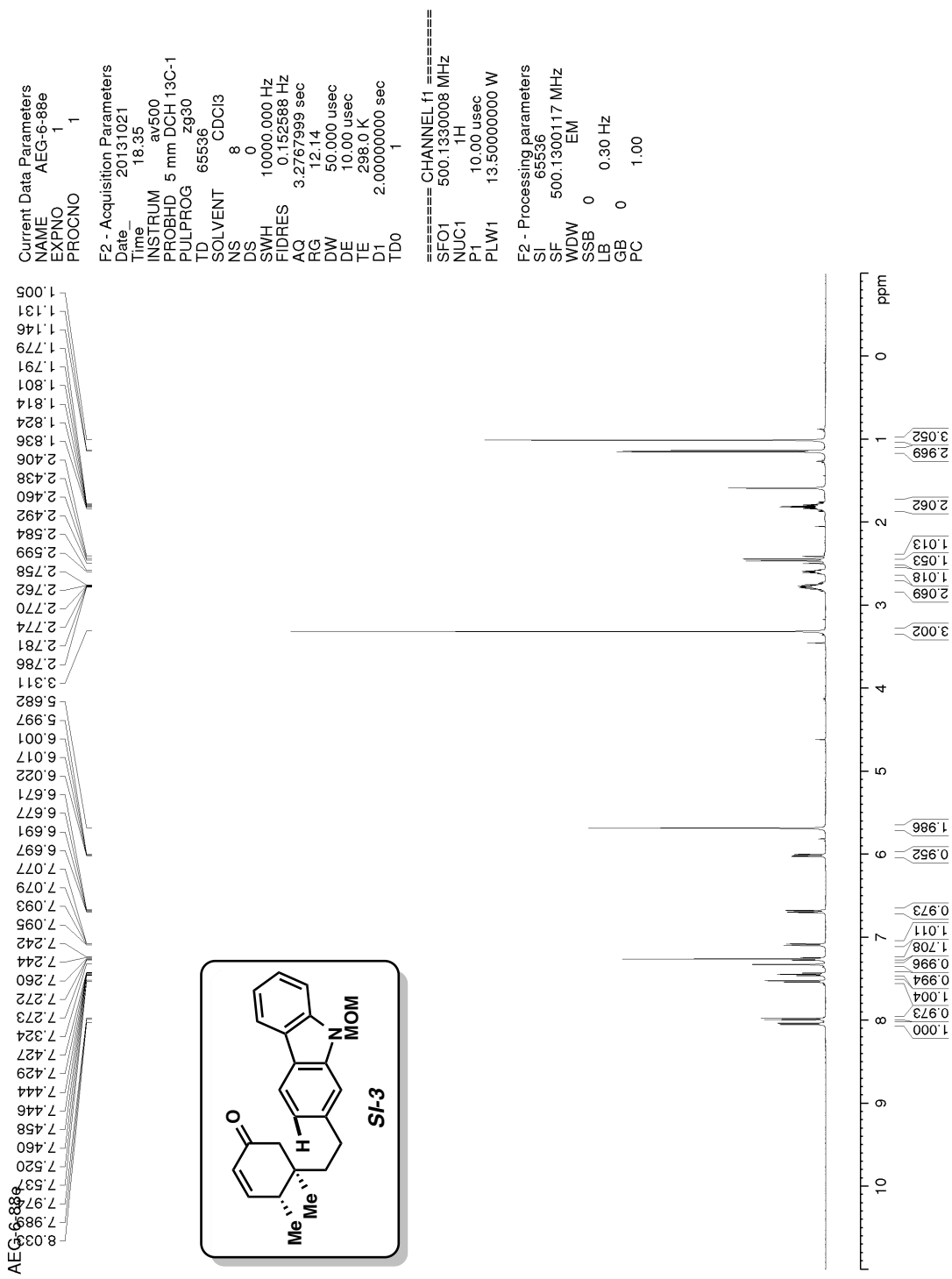
F2 - Processing parameters
SI      131072
SF      125.7577766 MHz
WDW     EM
SSB     0
LB      1.00 Hz
GB      0
PC      1.40
    
```

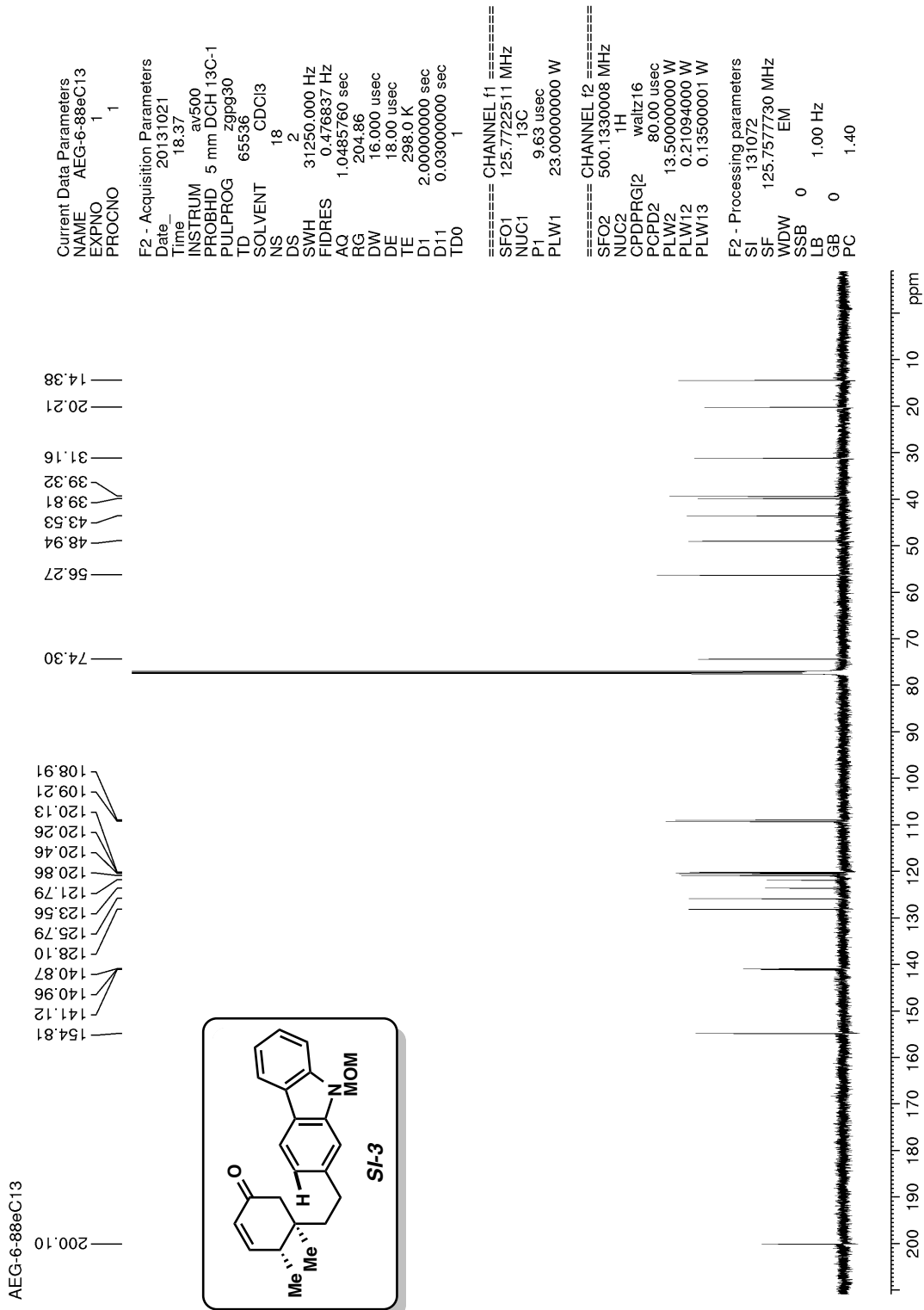


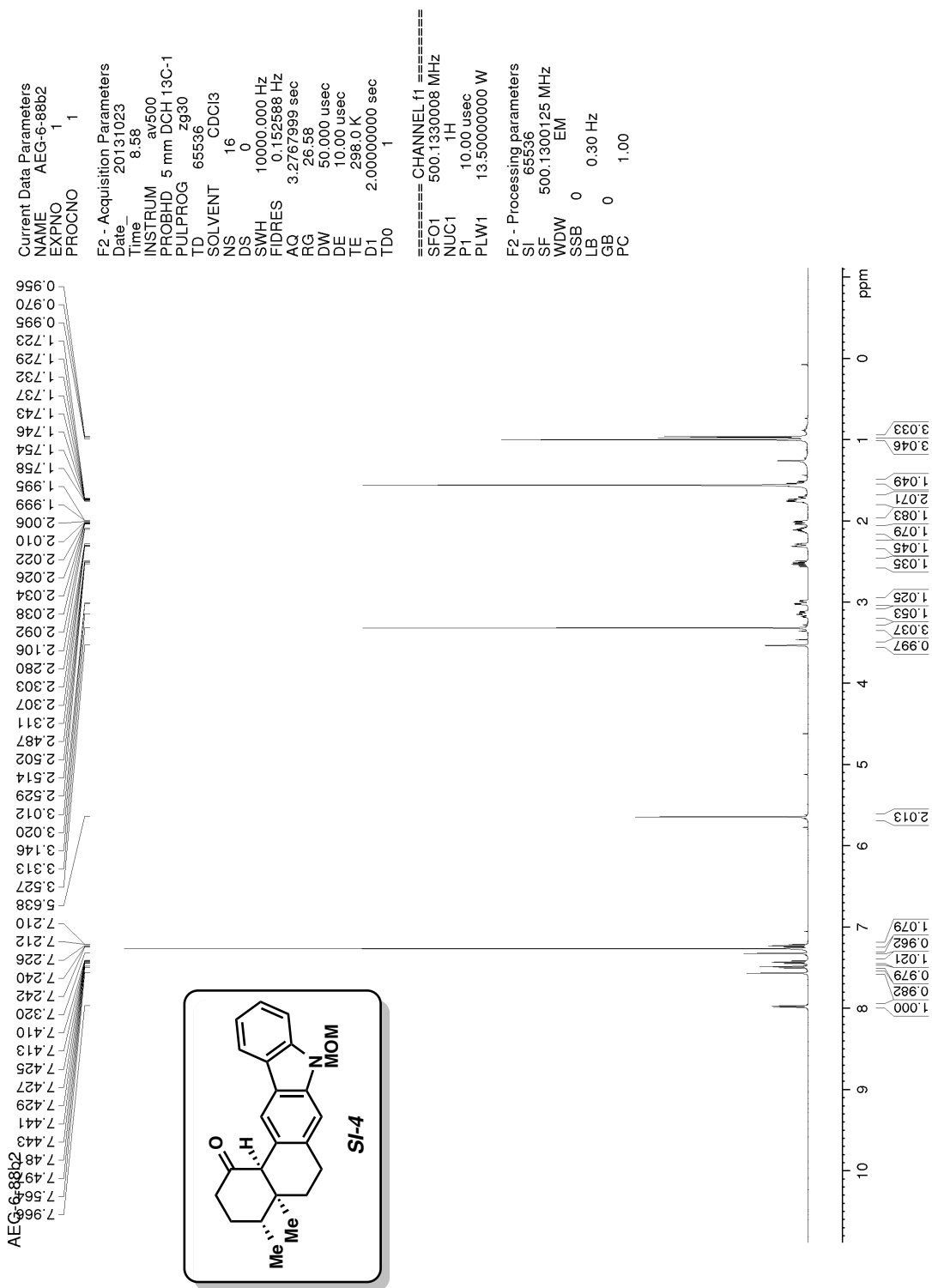




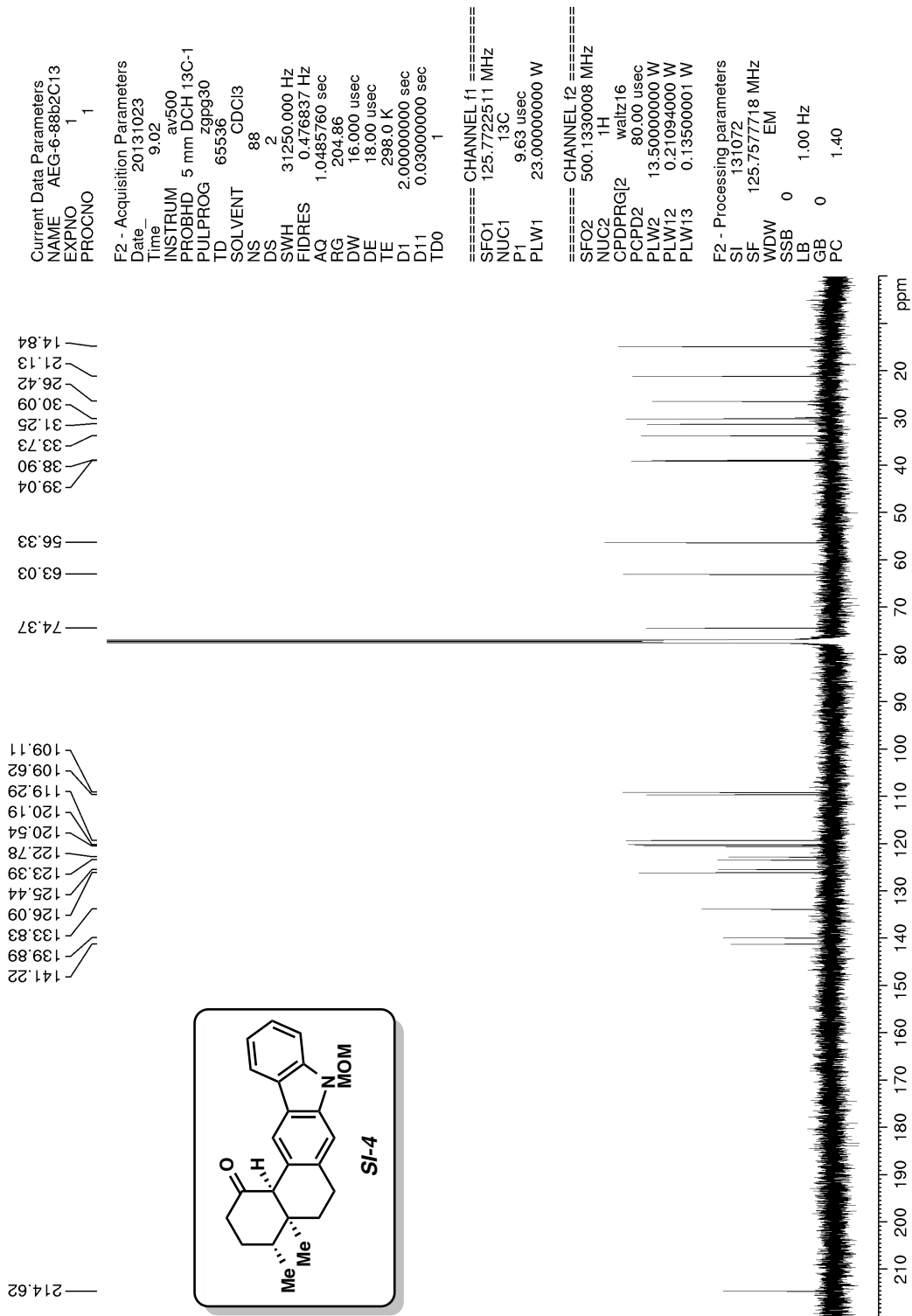


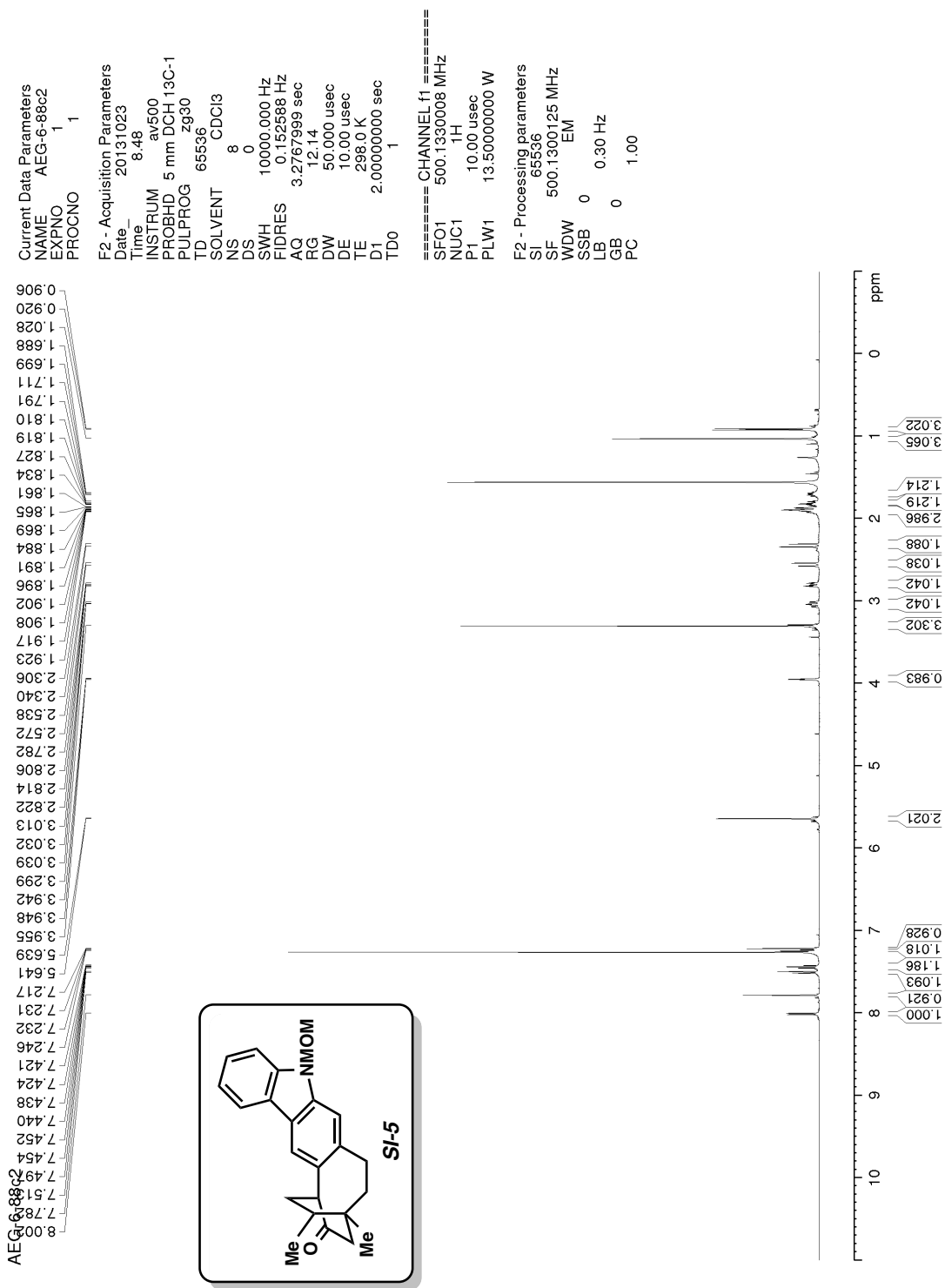




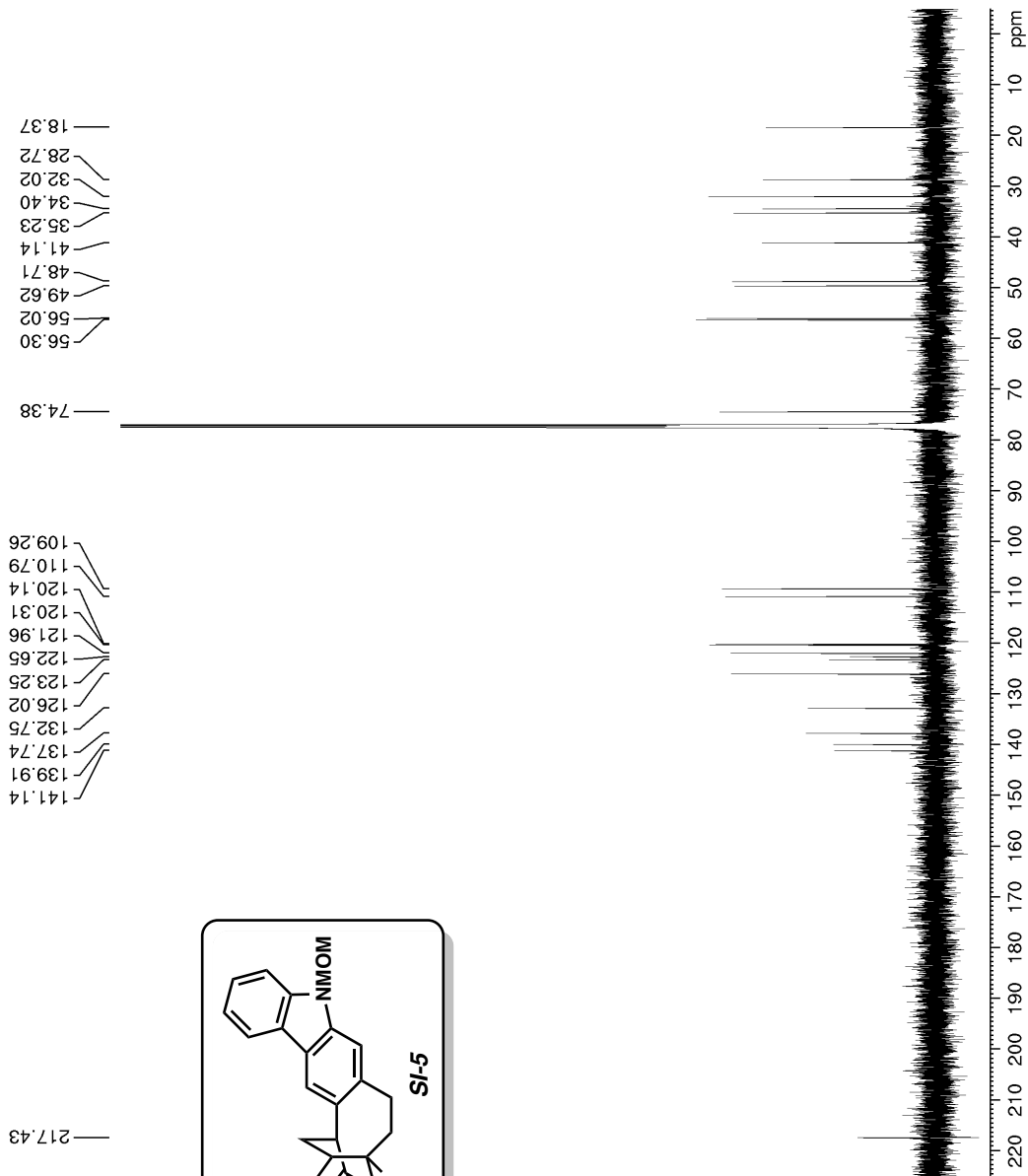


AEG-6-88b2C13





AEG-6-88c2C13



```

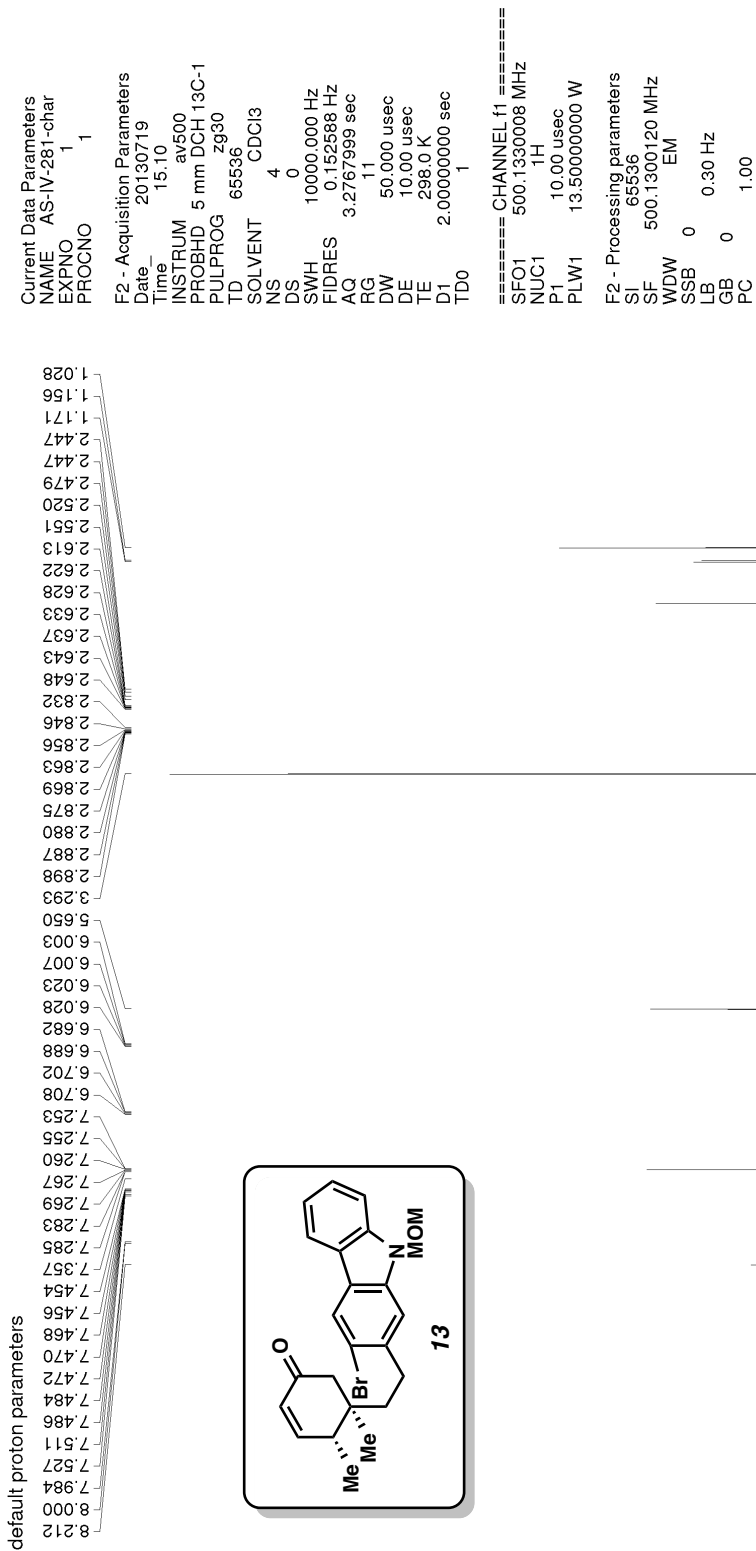
Current Data Parameters
NAME  AEG-6-88c2C13
EXPNO 1
PROCNO 1

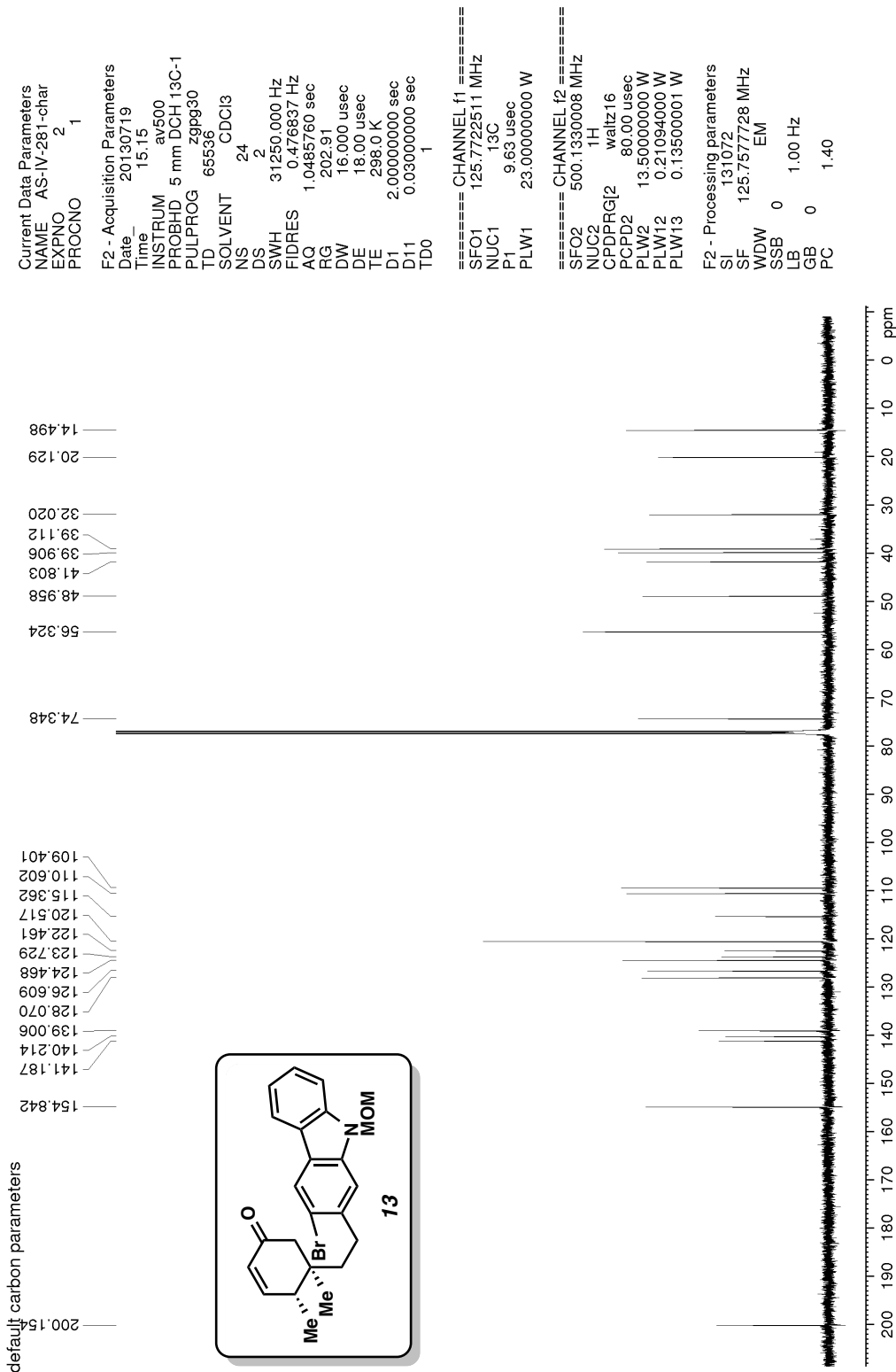
F2 - Acquisition Parameters
Date_ 20131023
Time_ 8.51
INSTRUM av500
PROBHD 5 mm DCH 13C-1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 72
DS 2
SWH 31250.000 Hz
FIDRES 0.476837 Hz
AQ 1.0485760 sec
RG 204.86
DW 16.000 usec
DE 18.00 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

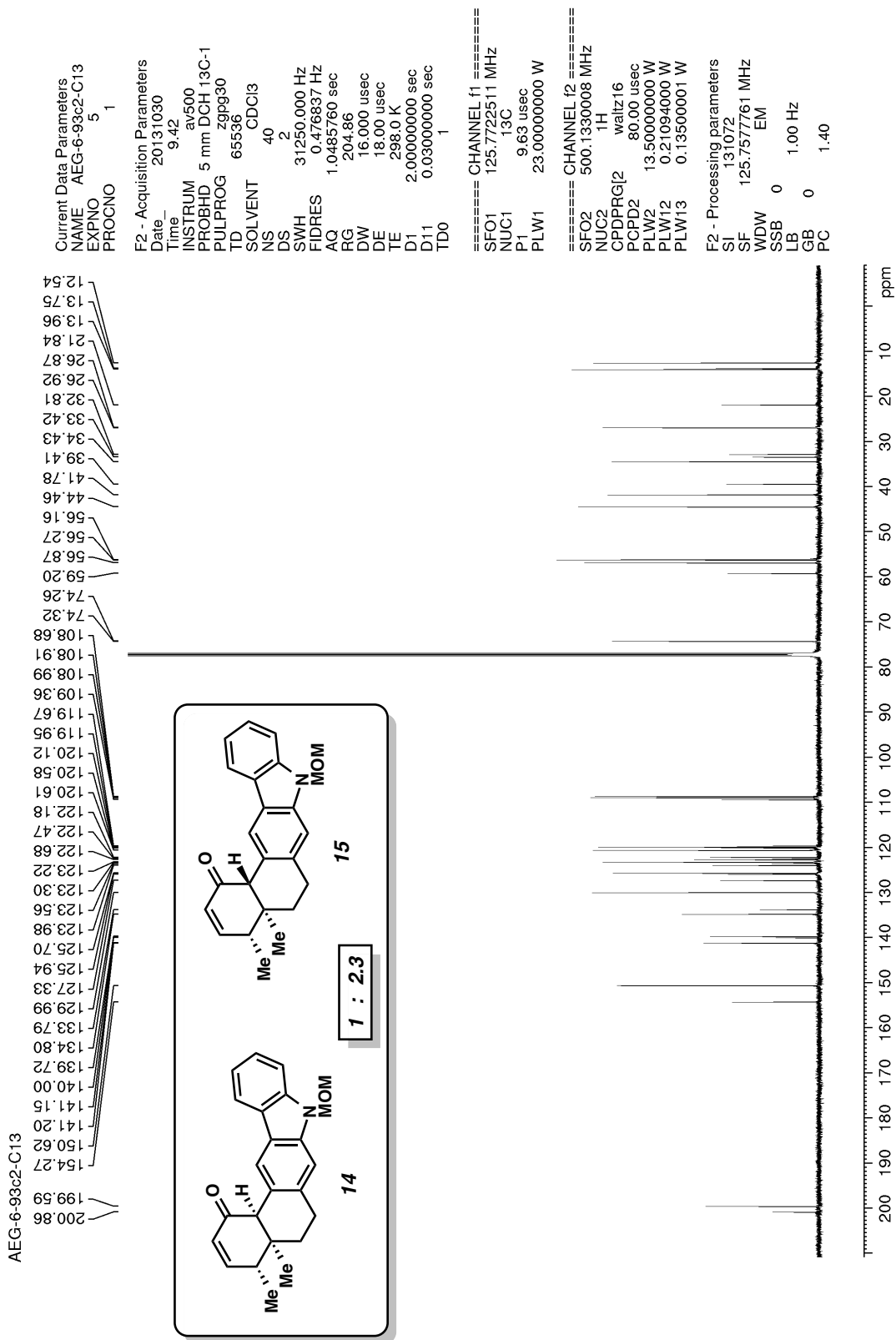
===== CHANNEL f1 =====
SFO1 125.7722511 MHz
NUC1 13C
P1 9.63 usec
PLW1 23.00000000 W

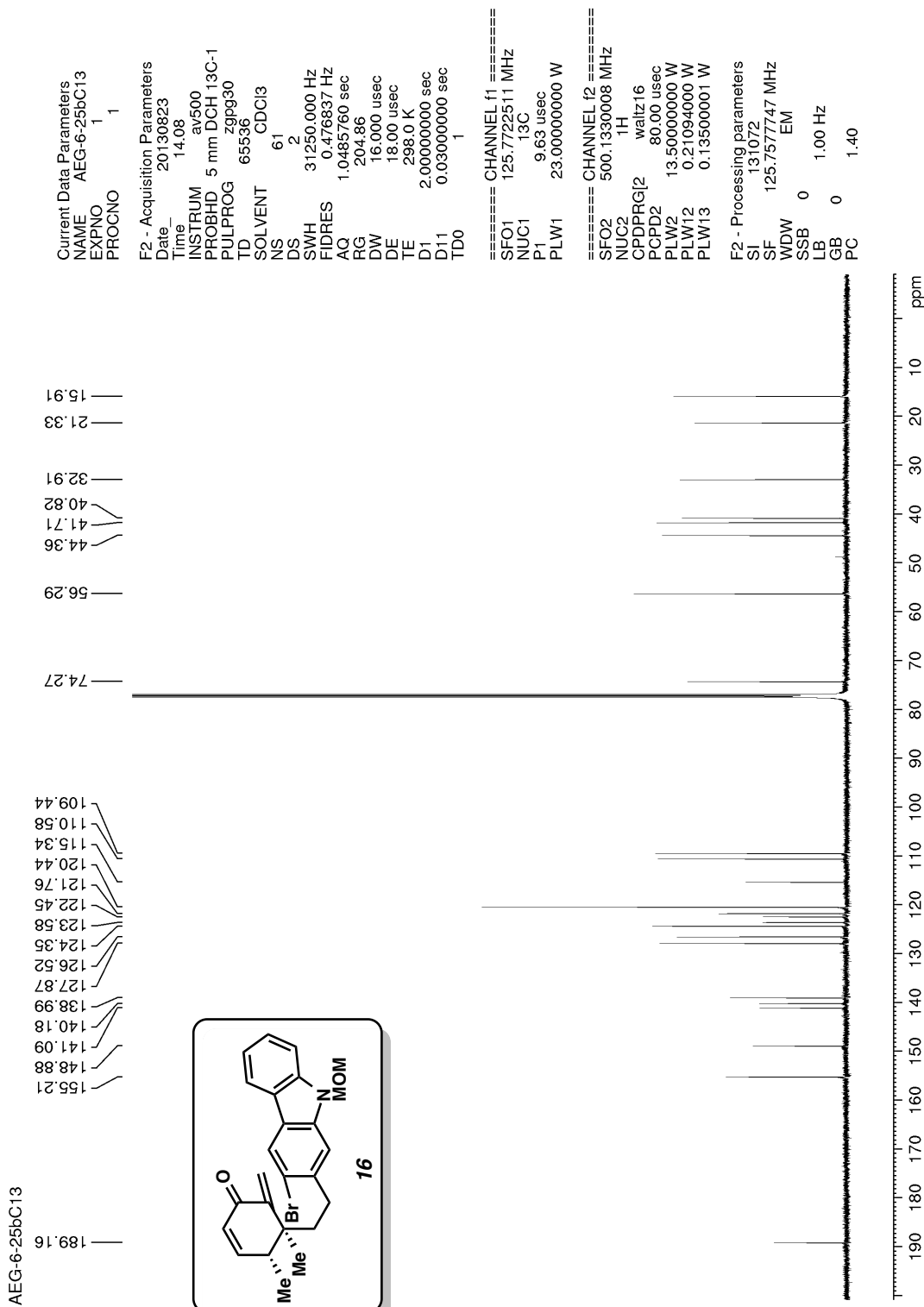
===== CHANNEL f2 =====
SFO2 500.1330008 MHz
NUC2 1H
CPDPRG2 waltz16
PCPD2 80.00 usec
PLW2 13.50000000 W
PLW12 0.21094000 W
PLW13 0.135000001 W

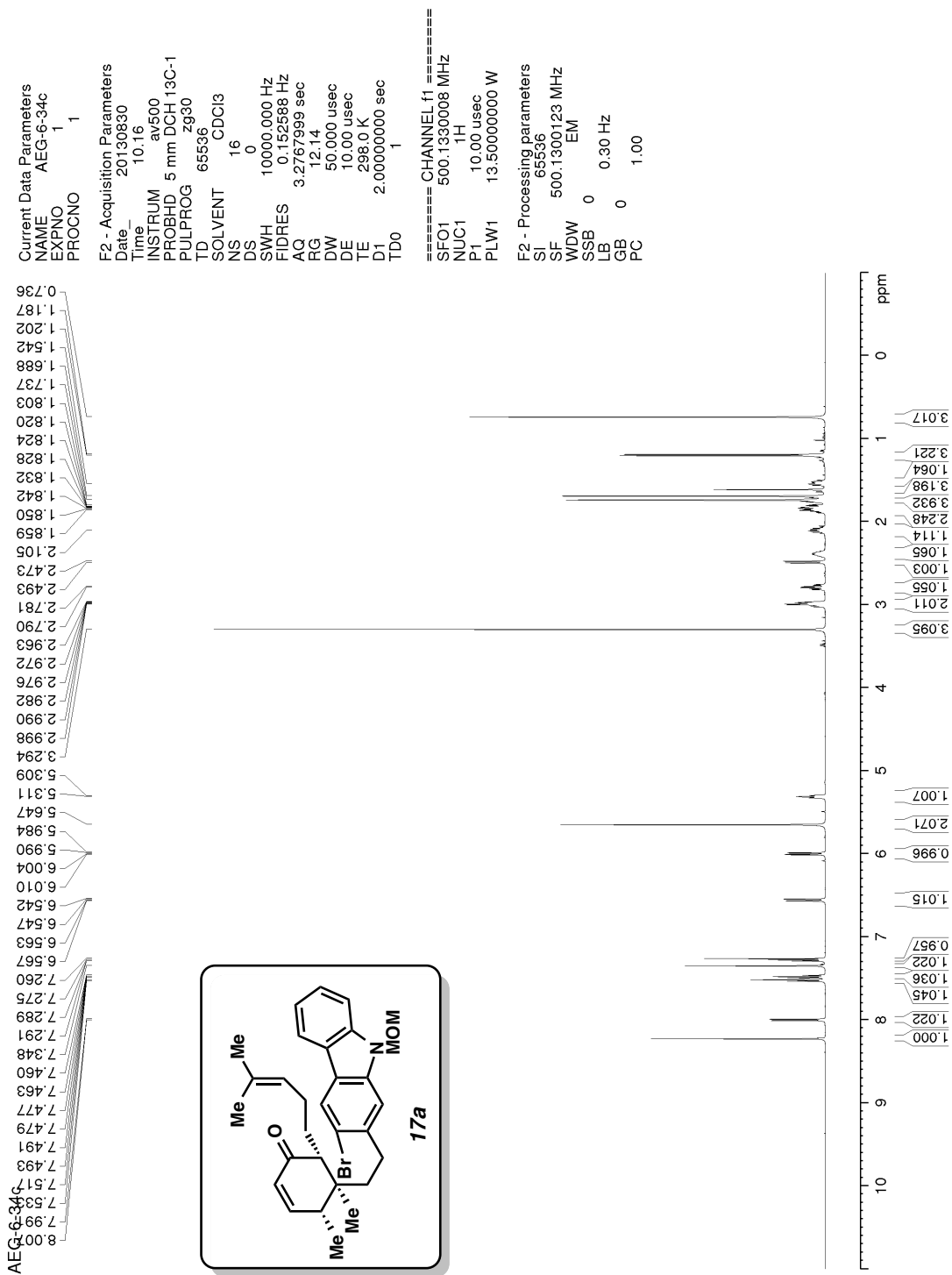
F2 - Processing parameters
SI 131072
SF 125.757719 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
    
```

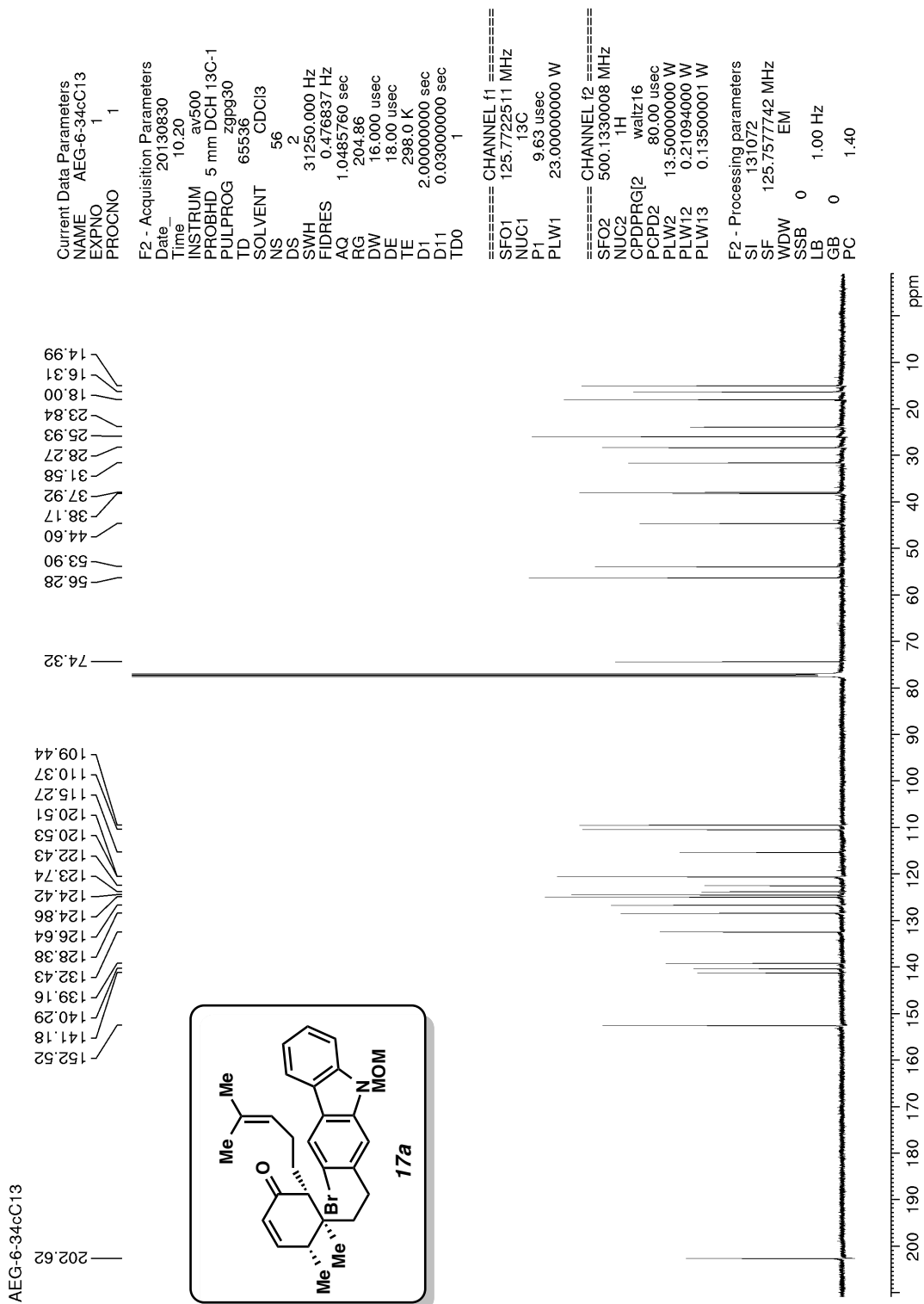


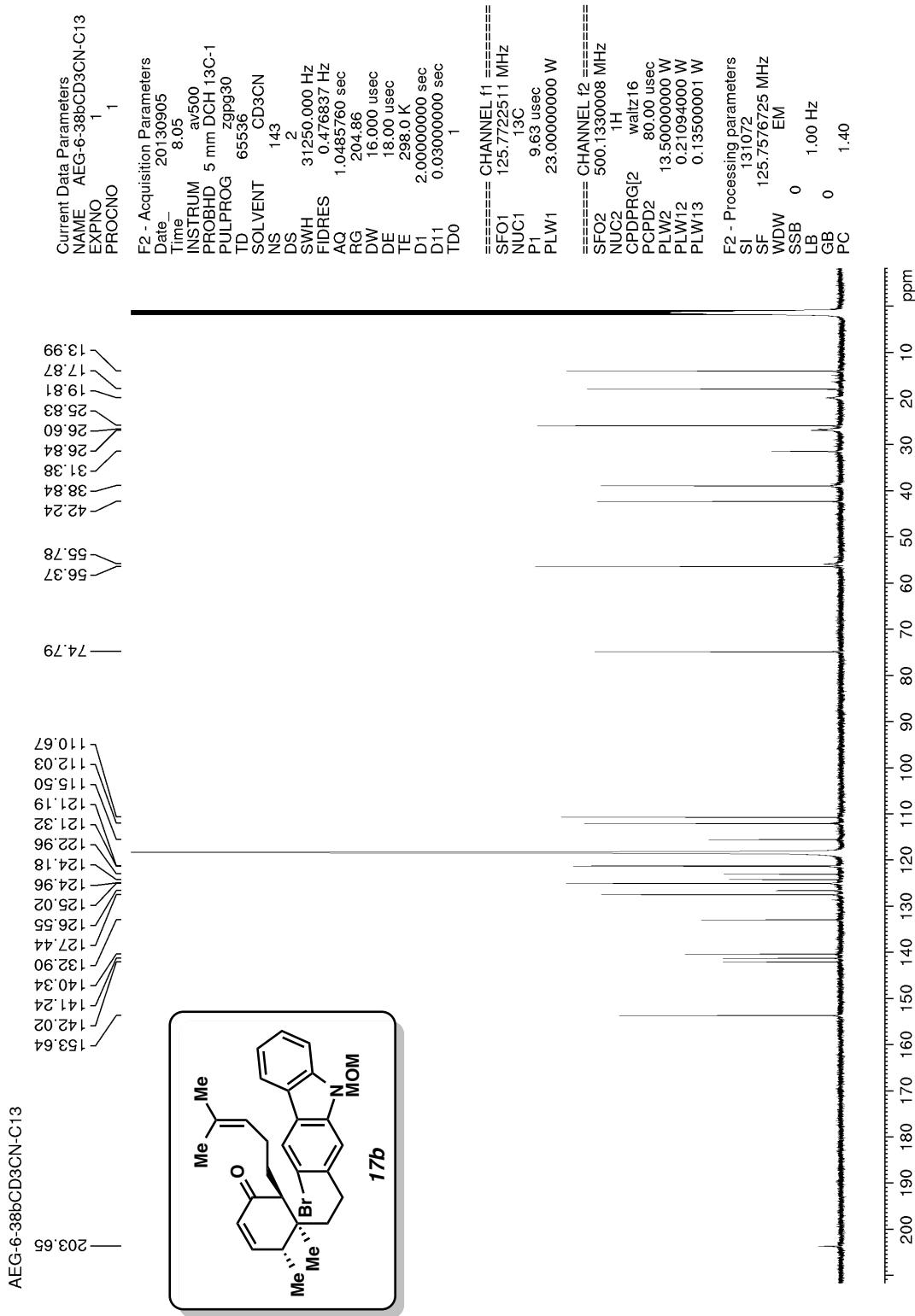












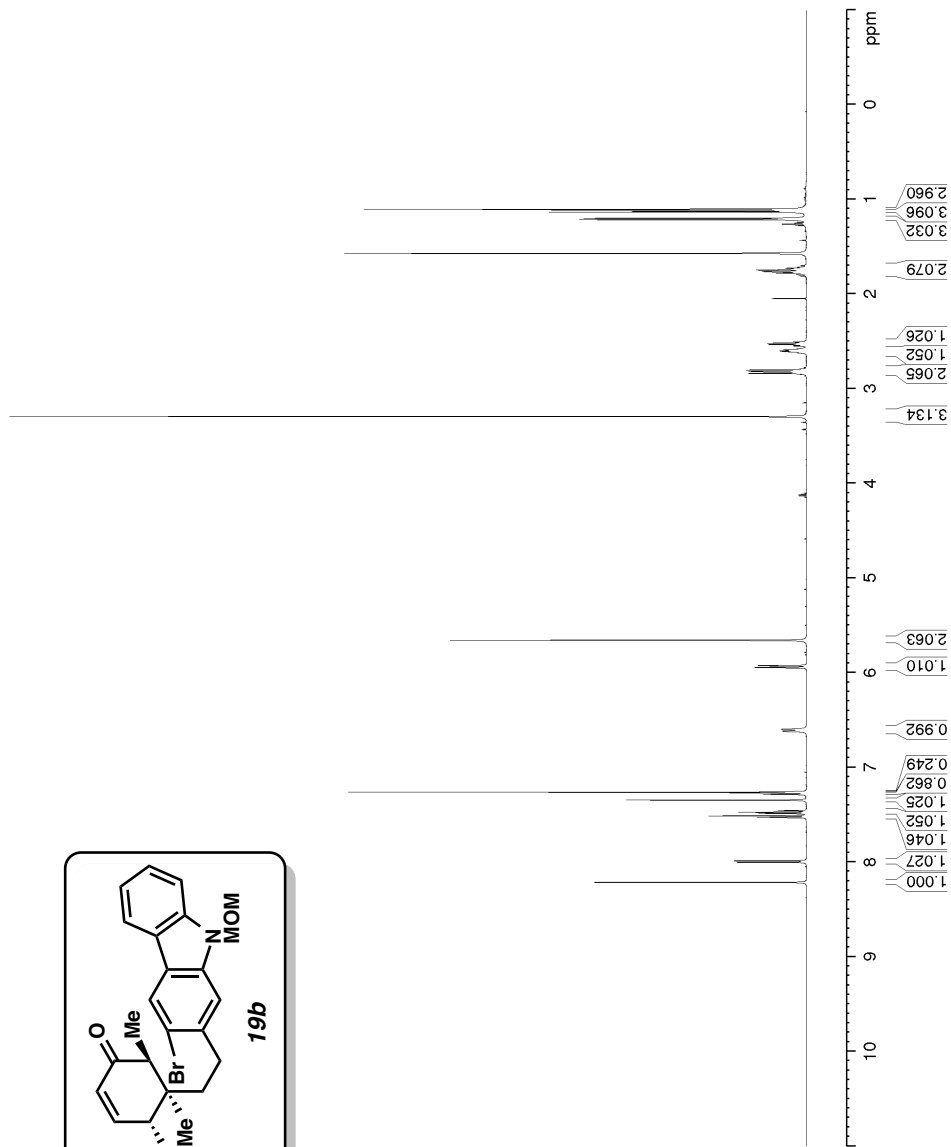
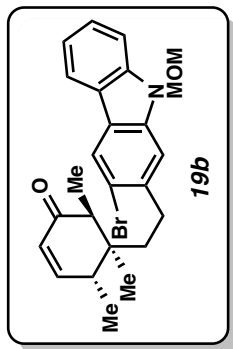
AEG-6-97c

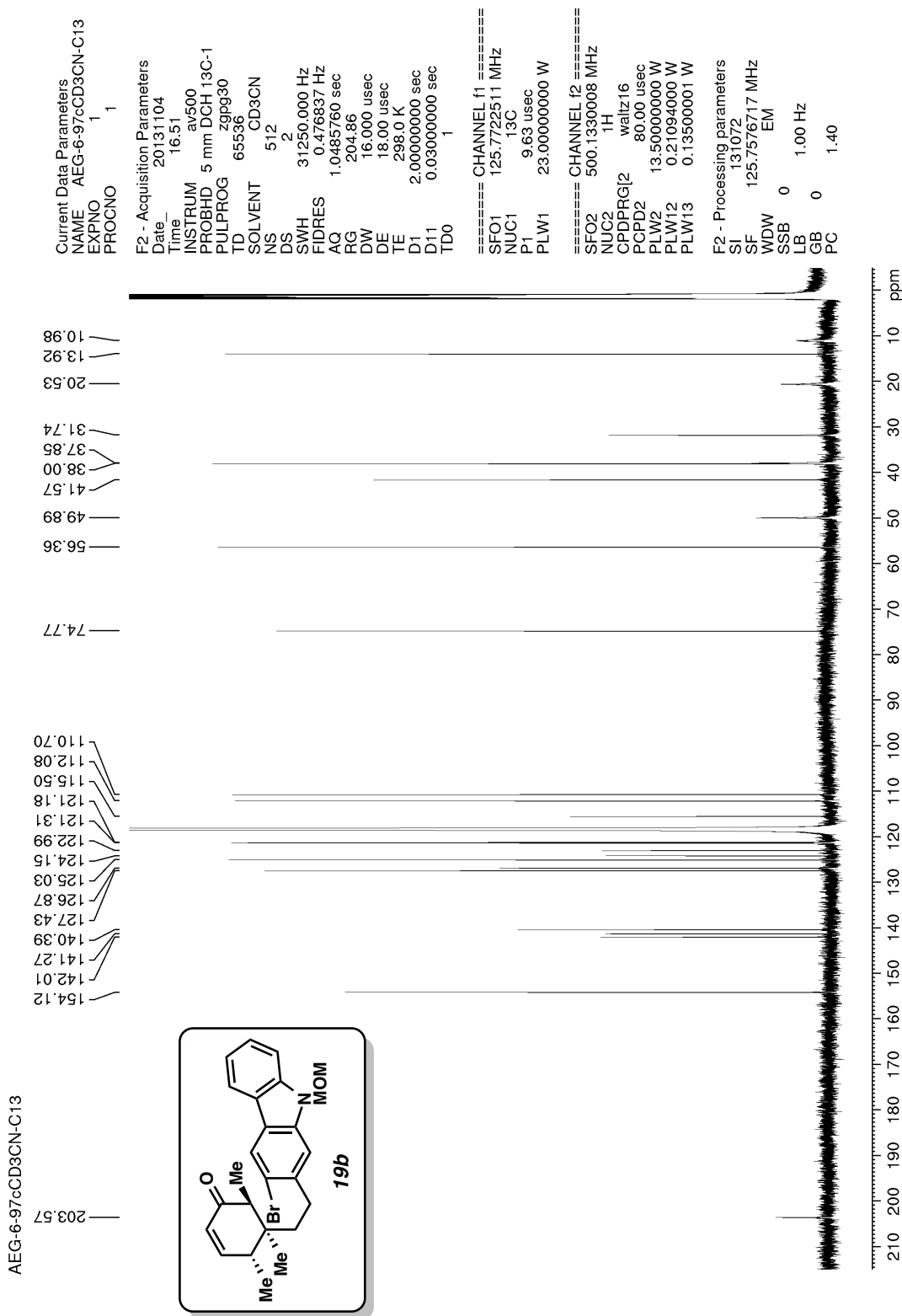
Current Data Parameters
 NAME AEG-6-97c
 EXPNO 1
 PROCNO 1

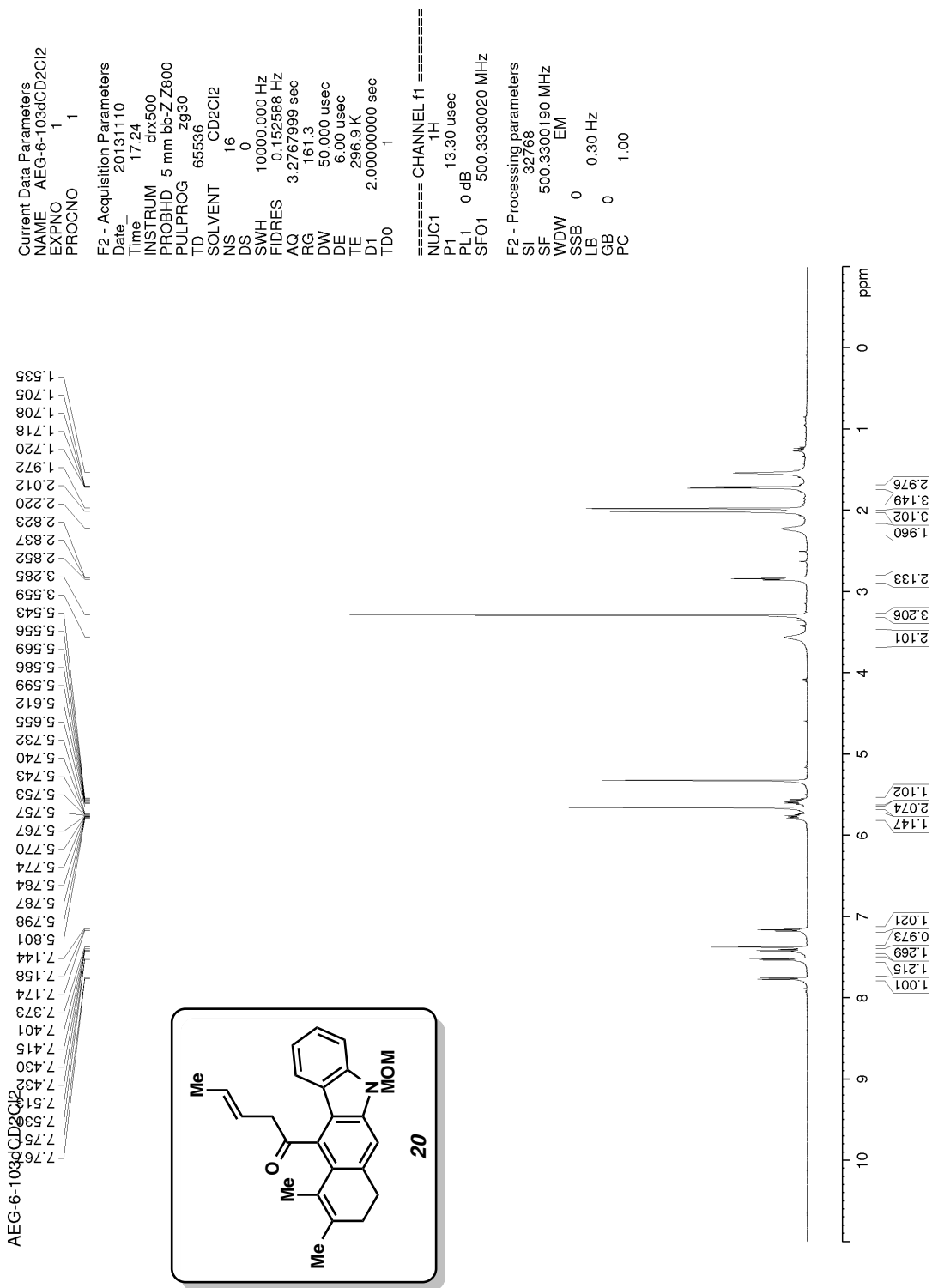
F2 - Acquisition Parameters
 Date_ 20131104
 Time 14.26
 INSTRUM av500
 PROBHD 5 mm DCH13C-1
 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 8
 DS 0
 SWH 10000.000 Hz
 FIDRES 0.152588 Hz
 AQ 3.2767999 sec
 RG 12.14
 DW 50.000 usec
 DE 10.00 usec
 TE 298.0 K
 D1 2.00000000 sec
 TD0 1

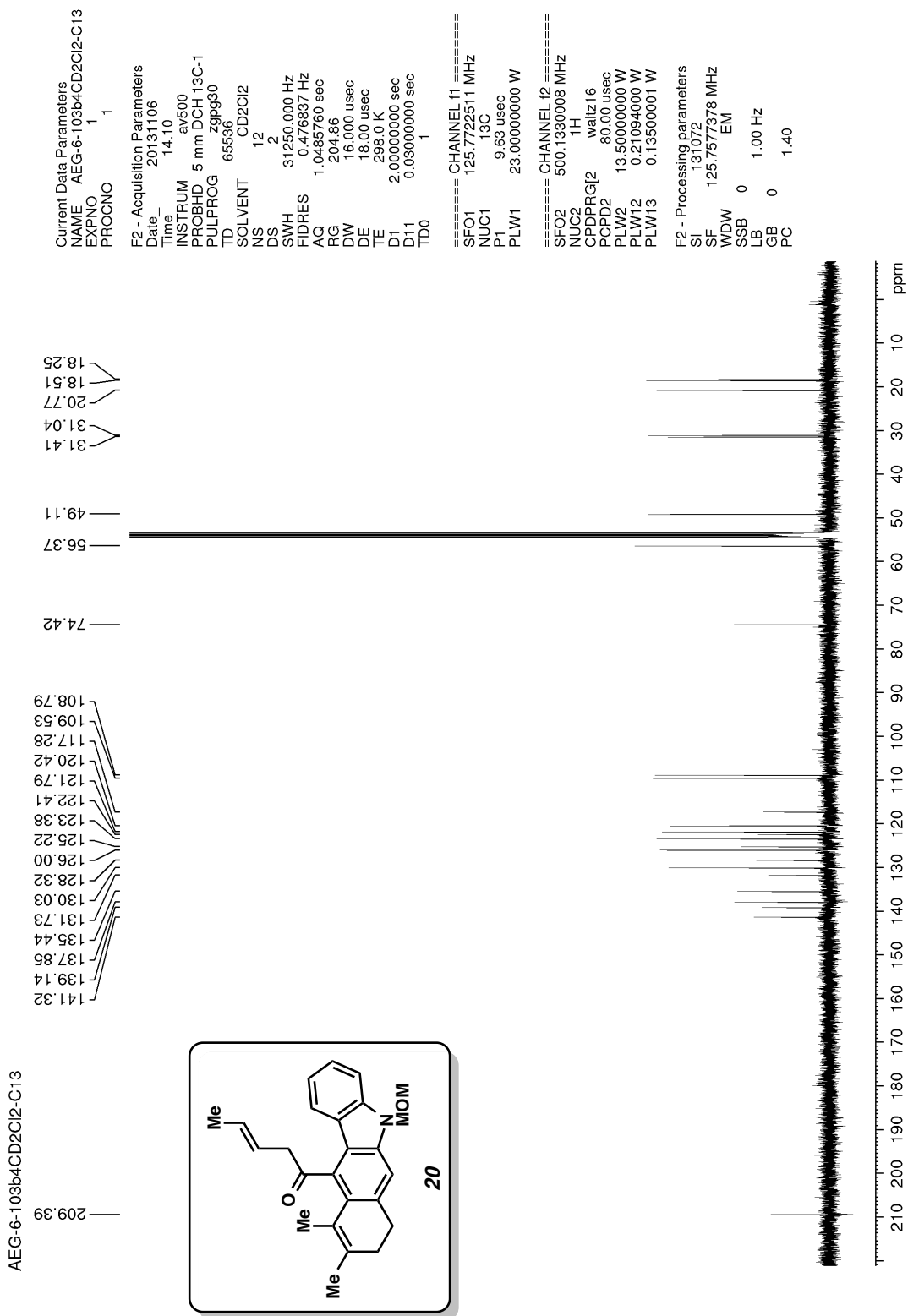
==== CHANNEL f1 =====
 SFO1 500.130008 MHz
 NUC1 1H
 P1 10.00 usec
 PLW1 13.50000000 W

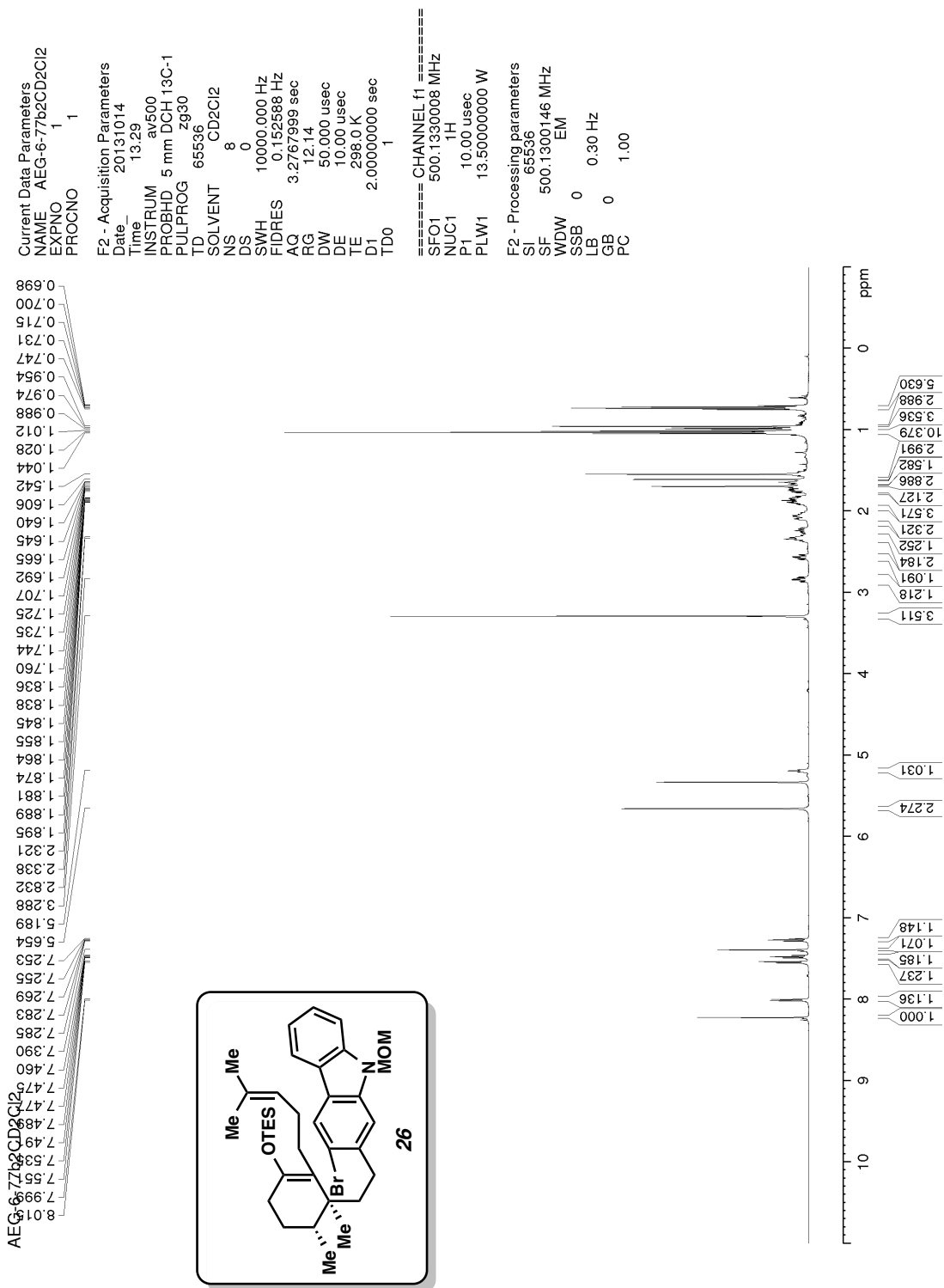
F2 - Processing parameters
 SI 65536
 SF 500.1300121 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00



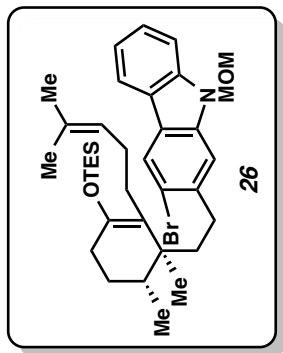
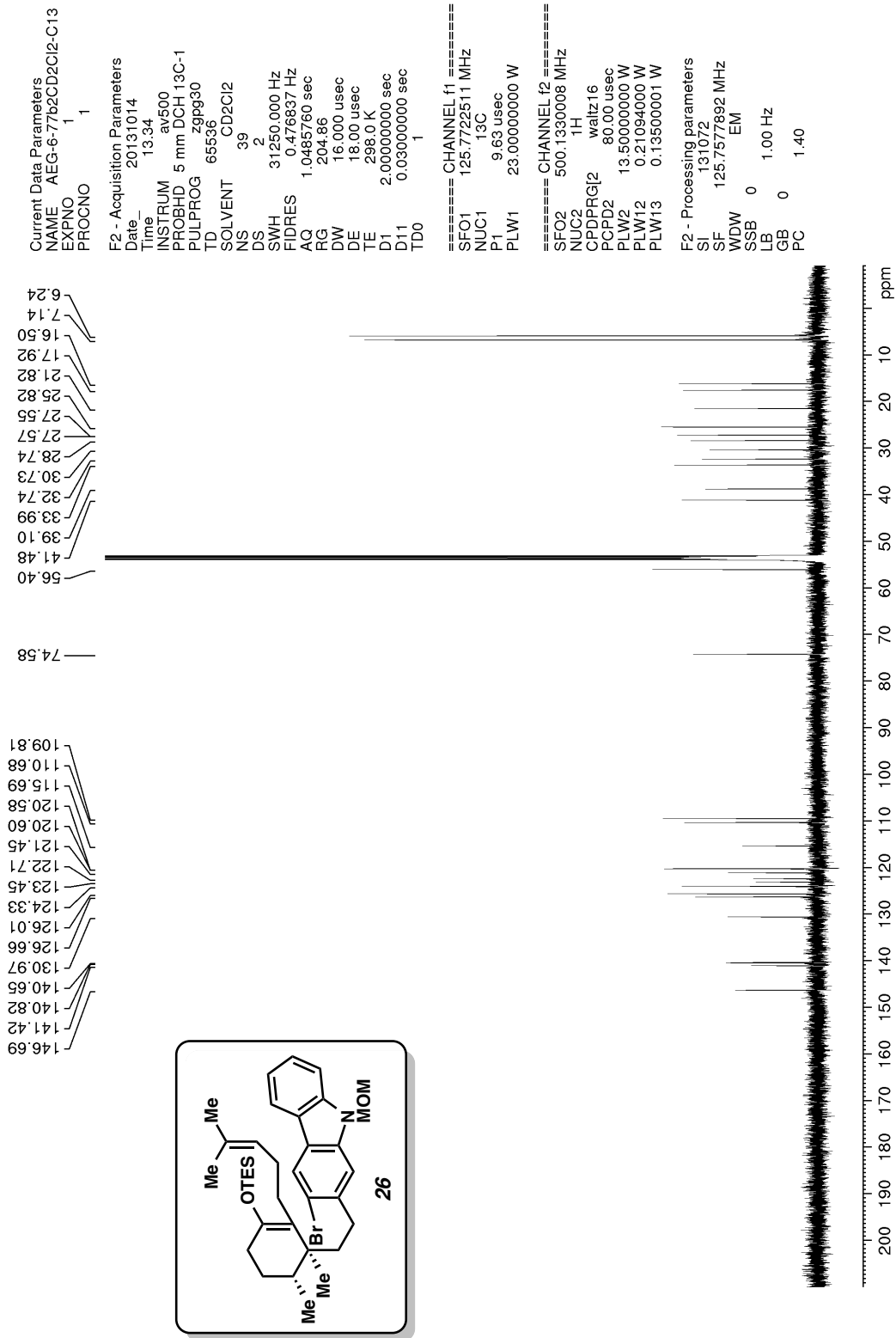








AEG-6-77b2CD2C12-C13



MAC-1-299-2

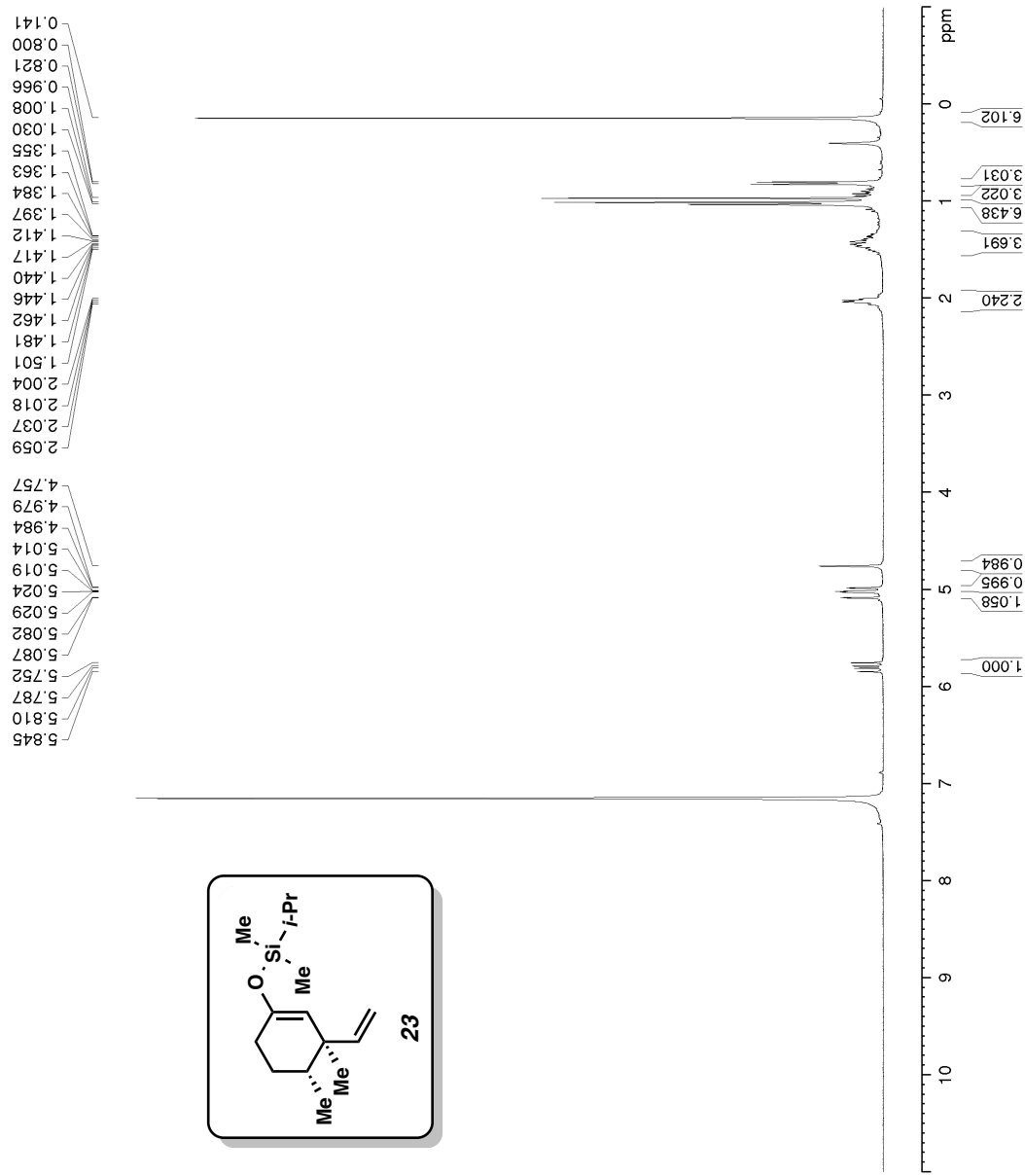
```

Current Data Parameters
NAME   MAC-1-299-2
EXPNO   1
PROCNO   1

F2 - Acquisition Parameters
Date_   20131117
Time    18.33
INSTRUM av300
PROBHD  5 mm PABBO BB-
PULPROG zg30
TD      65536
SOLVENT C6D6
NS      24
DS      0
SWH     5995.204 Hz
FIDRES  0.091480 Hz
AQ      5.4657025 sec
RG      362
DW      83.400 usec
DE      6.00 usec
TE      297.8 K
D1      2.0000000 sec
TD0     1

===== CHANNEL f1 =====
NUC1    1H
P1      16.00 usec
PL1     0 dB
PL1W    9.31909847 W
SFO1    300.1318008 MHz

F2 - Processing parameters
SI      65536
SF      300.1300384 MHz
WDW     EM
SSB     0
LB      0.30 Hz
GB      0
PC      1.40
    
```



default carbon parameters

151.02
149.72

112.88
112.27

42.22

37.42

30.20

27.83

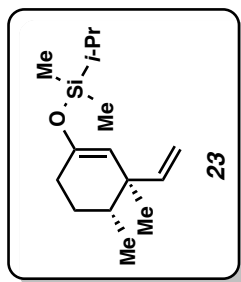
21.71

17.59

16.11

15.82

-2.79
-2.82



```

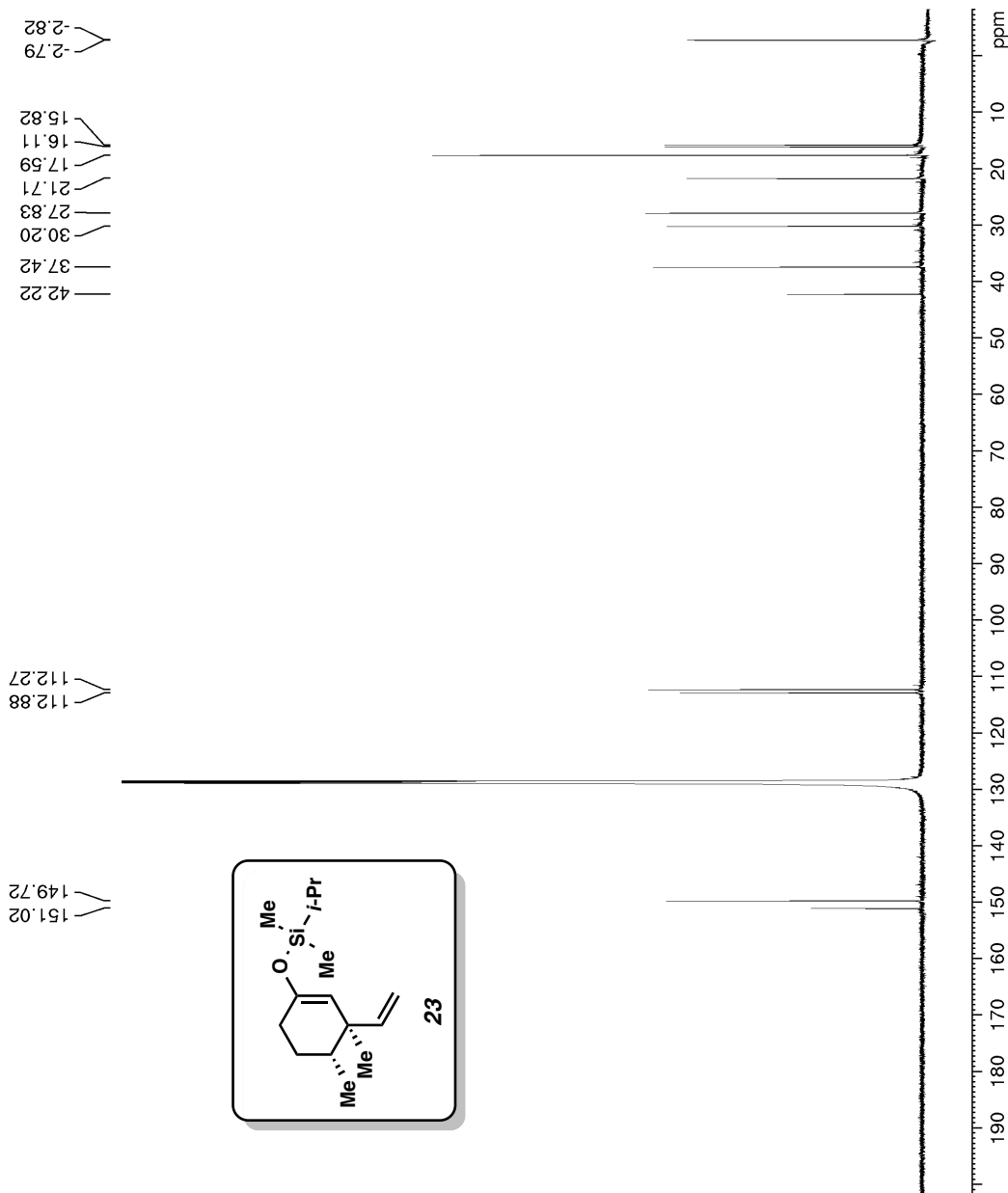
Current Data Parameters
NAME MAC-1-299-g 13C
EXPNO 1
PROCNO 1

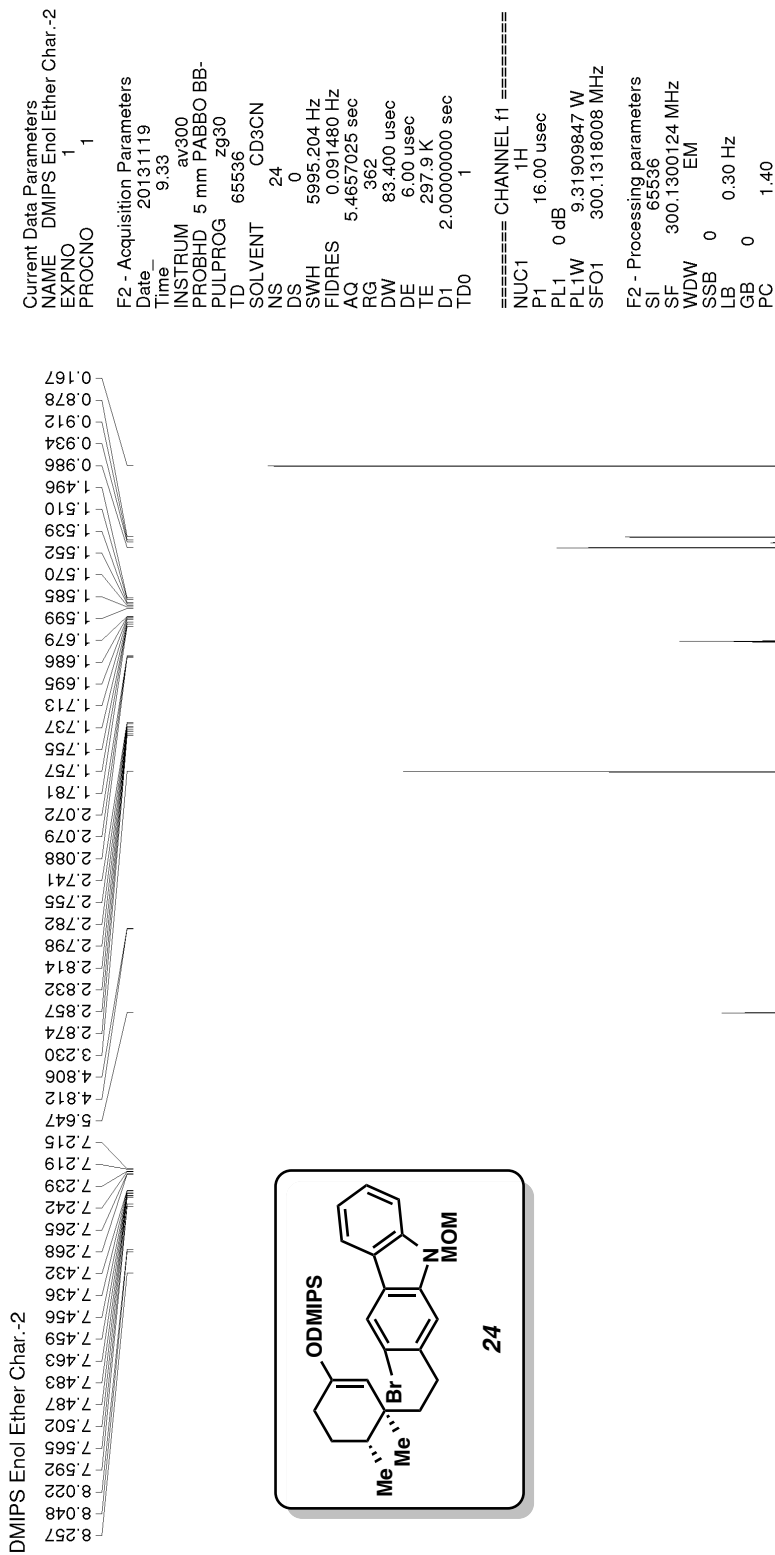
F2 - Acquisition Parameters
Date_ 20131125
Time 13.56
INSTRUM av500
PROBHD 5 mm DCH 13C-1
PULPROG zgpg30
TD 65536
SOLVENT C6D6
NS 80
DS 2
SWH 31250.000 Hz
FIDRES 0.476837 Hz
AQ 1.0485760 sec
RG 204.86
DW 16.000 usec
DE 18.000 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

===== CHANNEL f1 =====
SFO1 125.772511 MHz
NUC1 13C
P1 9.63 usec
PLW1 23.00000000 W

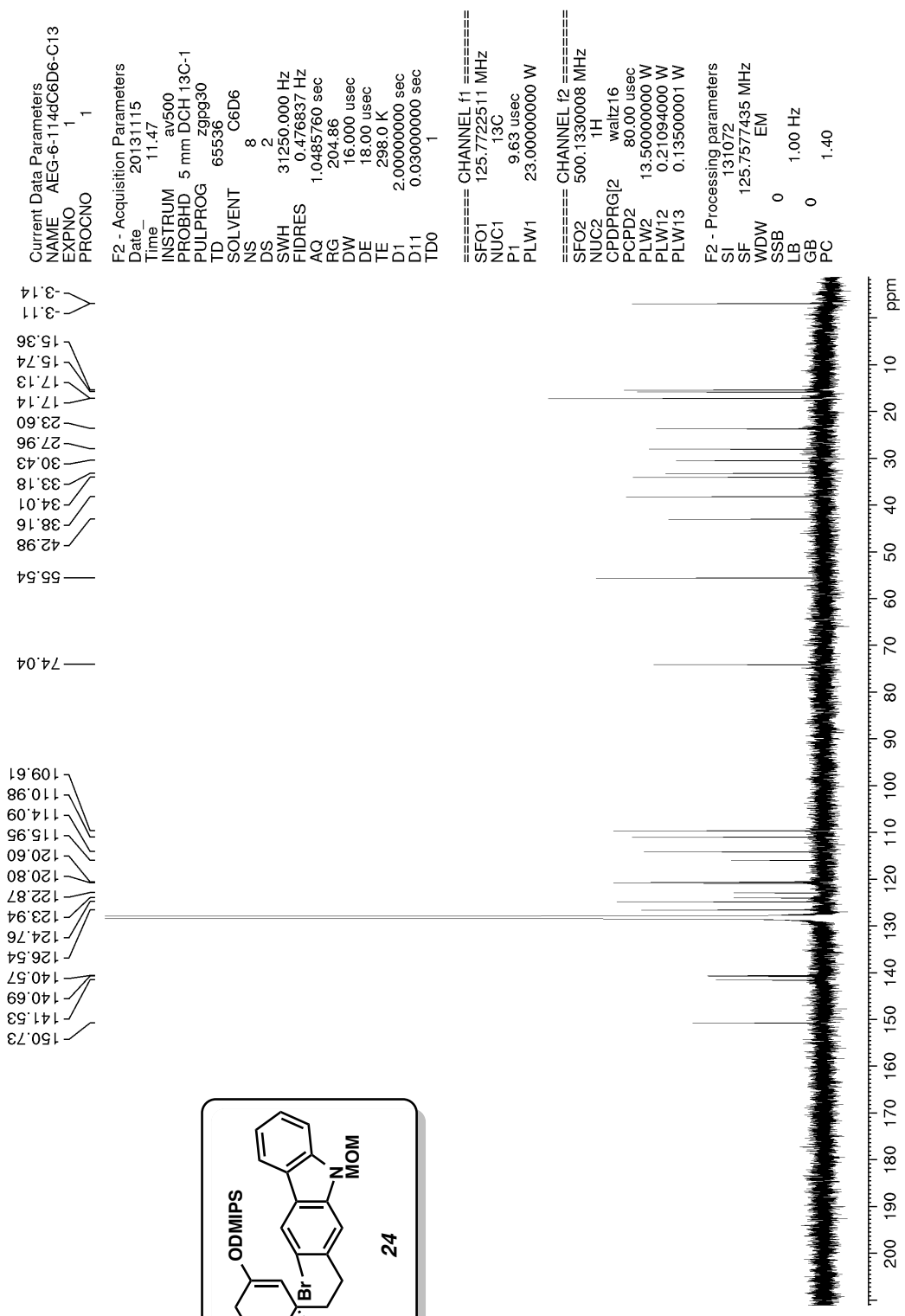
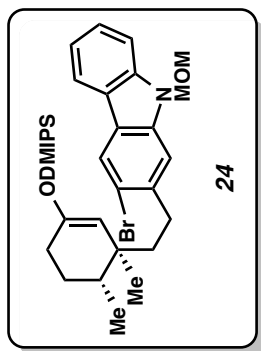
===== CHANNEL f2 =====
SFO2 500.1330008 MHz
NUC2 1H
CPDPRG2 waltz16
PCPD2 80.00 usec
PLW2 13.50000000 W
PLW12 0.21094000 W
PLW13 0.135000001 W

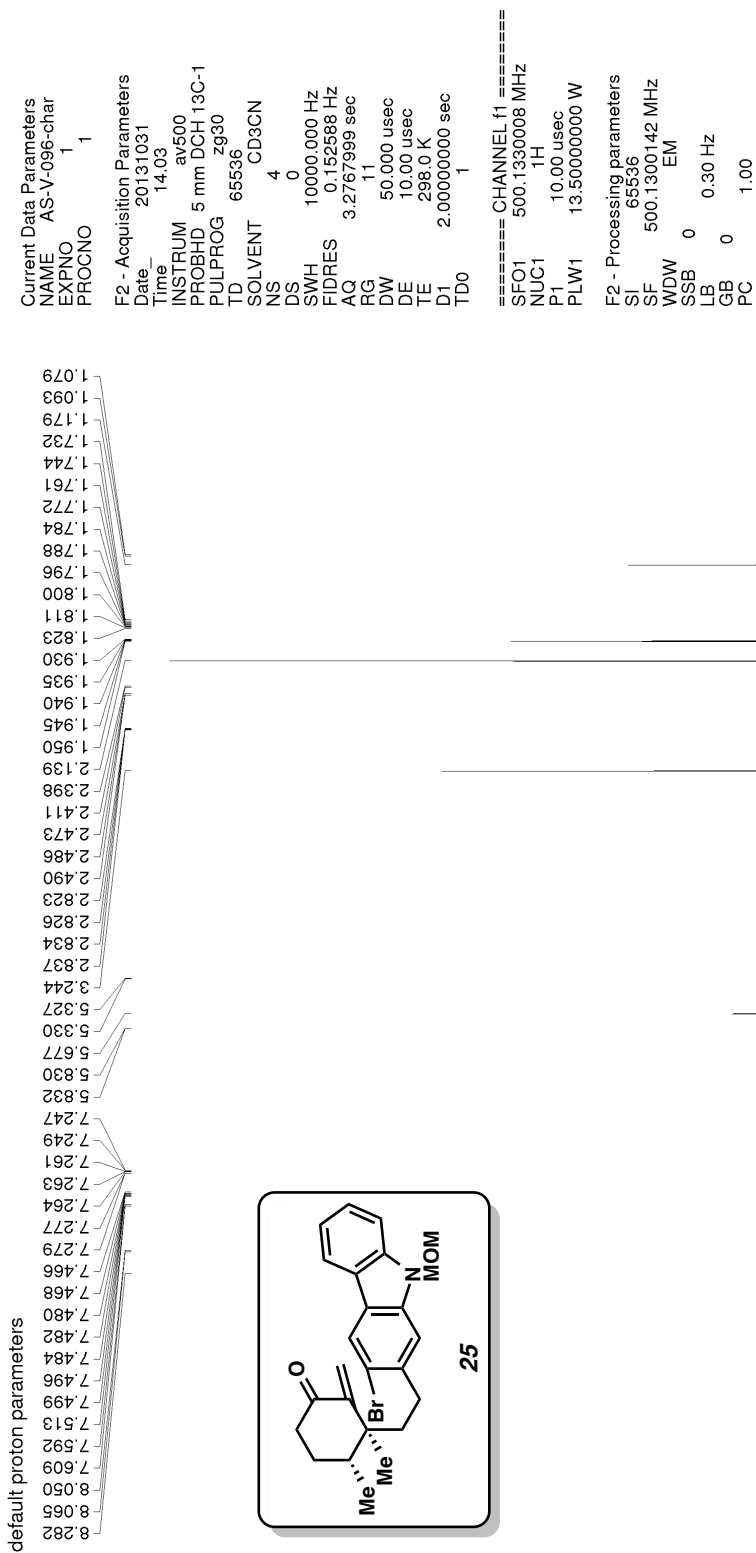
F2 - Processing parameters
SI 131072
SF 125.7576724 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
    
```

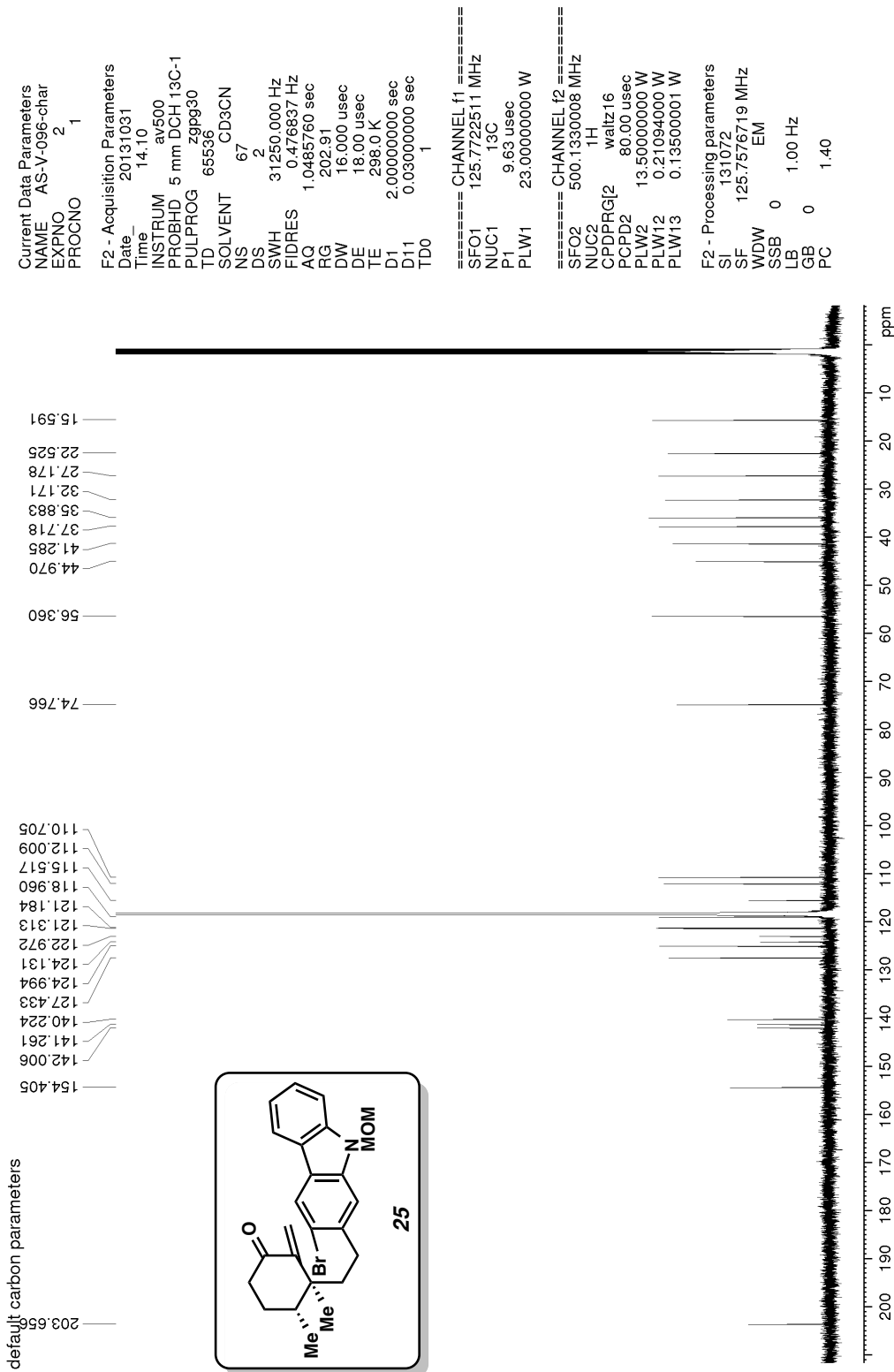


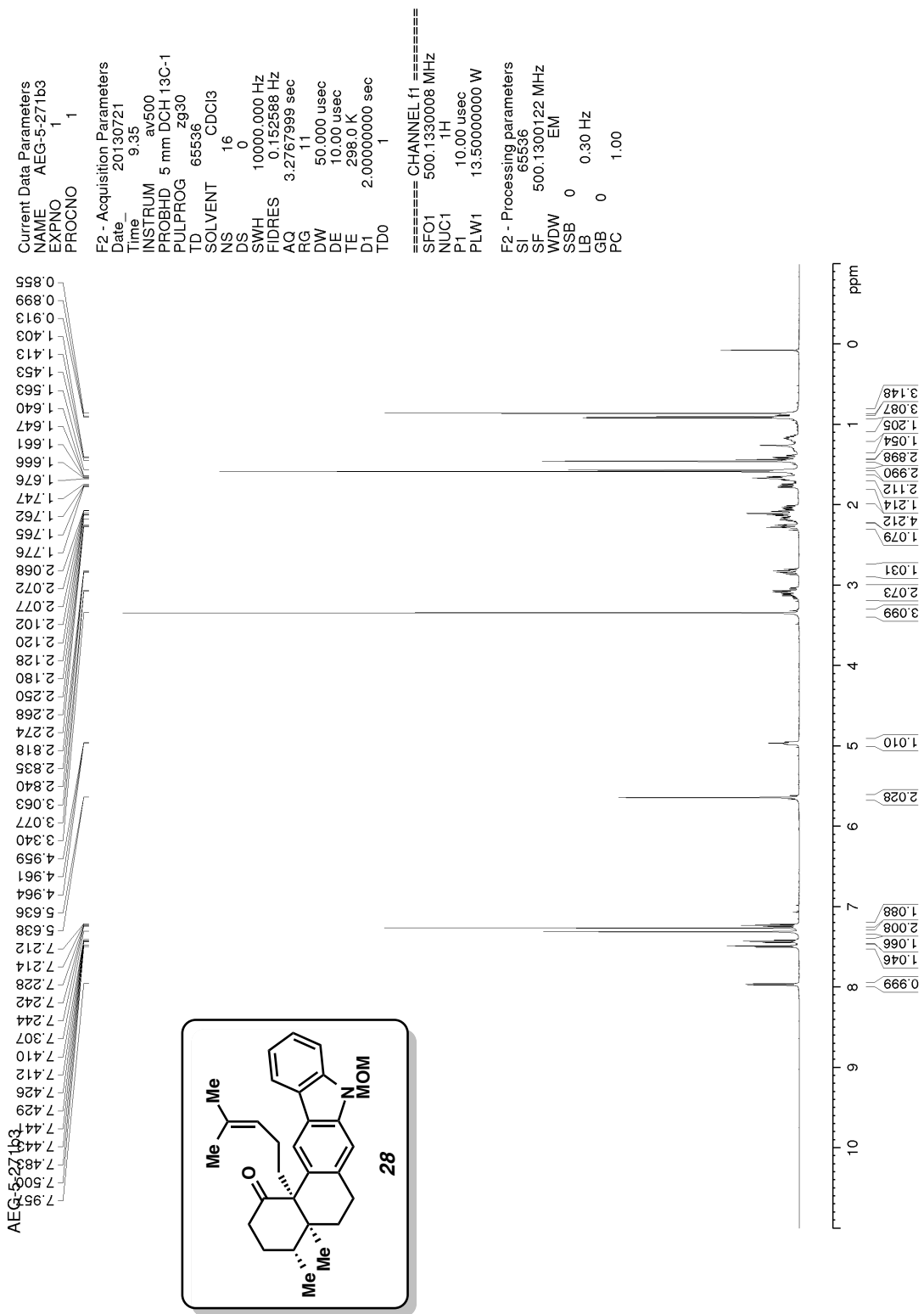


AEG-6-114dC6D6-C13

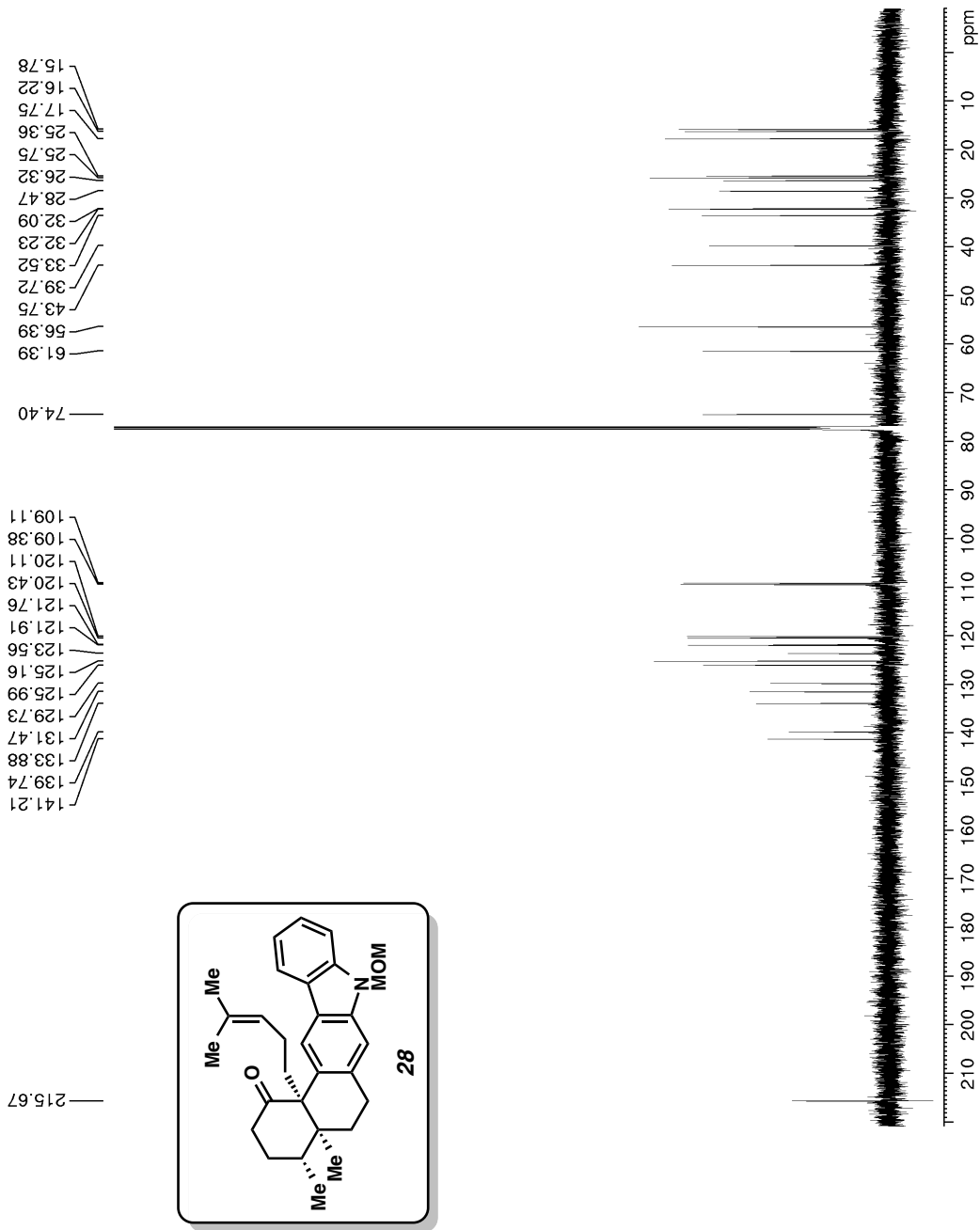








AEG-5-271b3C13-2



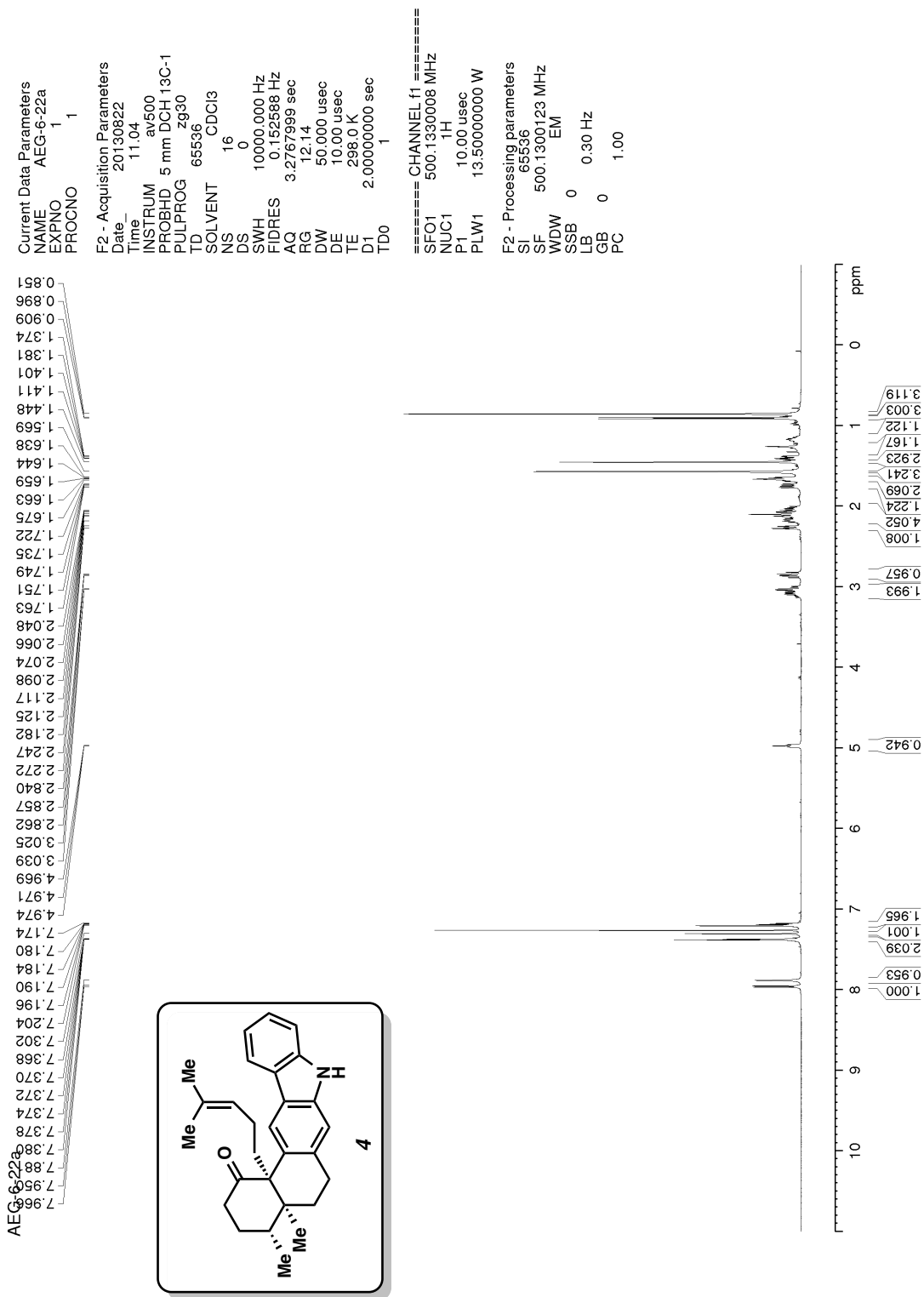
Current Data Parameters
 NAME AEG-5-271b3C13-2
 EXPNO 1
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20130721
 Time_ 9.40
 INSTRUM av500
 PROBHD 5 mm DCH 13C-1
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 12
 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

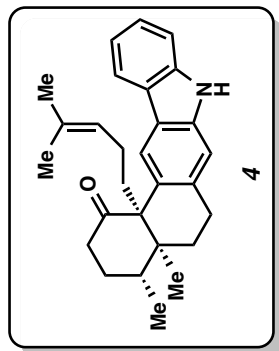
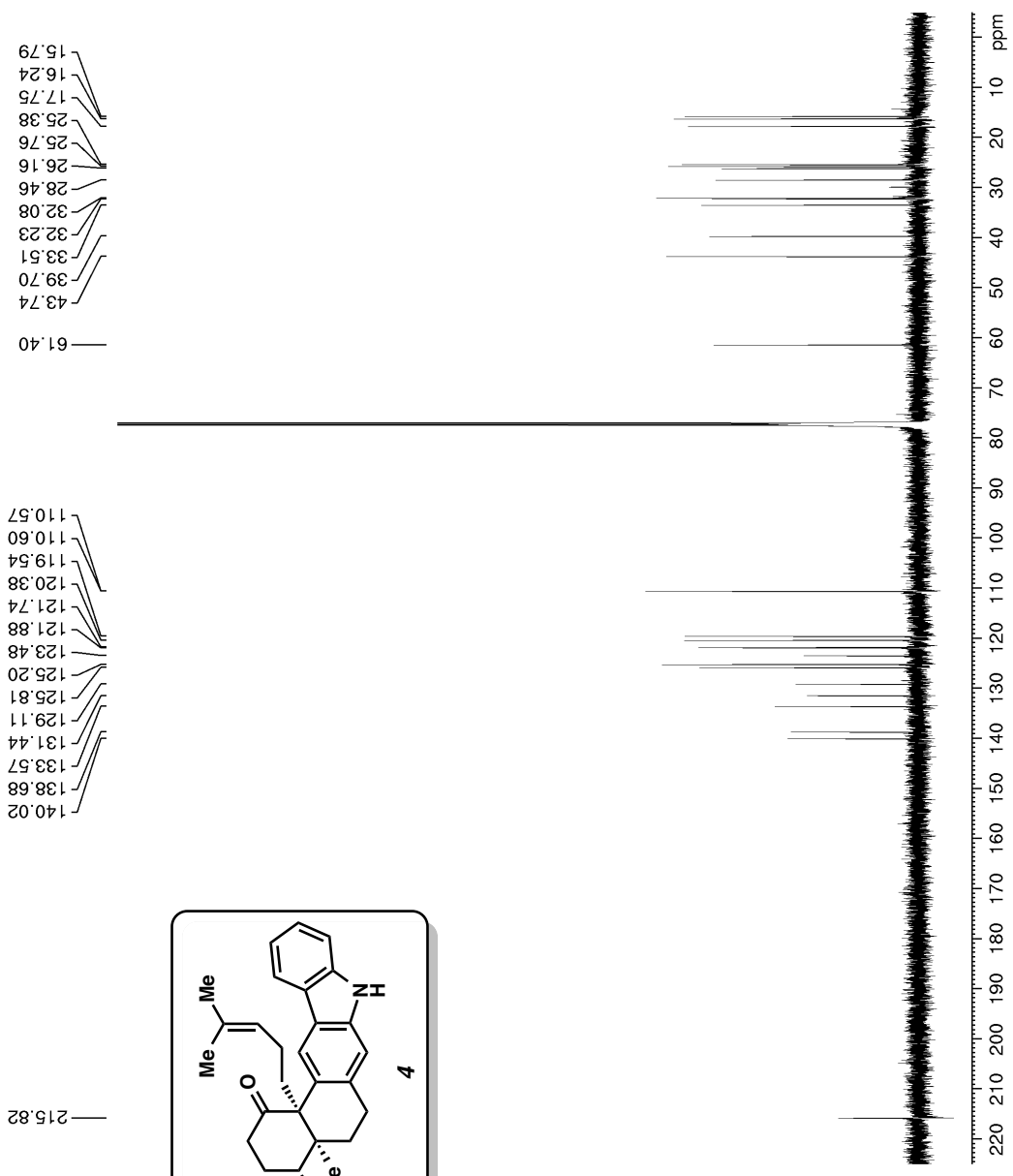
==== CHANNEL f1 =====
 SFO1 125.7722511 MHz
 NUC1 13C
 P1 9.63 usec
 PLW1 23.00000000 W

==== CHANNEL f2 =====
 SFO2 500.1330008 MHz
 NUC2 1H
 CPDPRG2 waltz16
 PCPD2 80.00 usec
 PLW2 13.50000000 W
 PLW12 0.21094000 W
 PLW13 0.13500001 W

F2 - Processing parameters
 SI 131072
 SF 125.757727 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40



AEG-6-22aC13



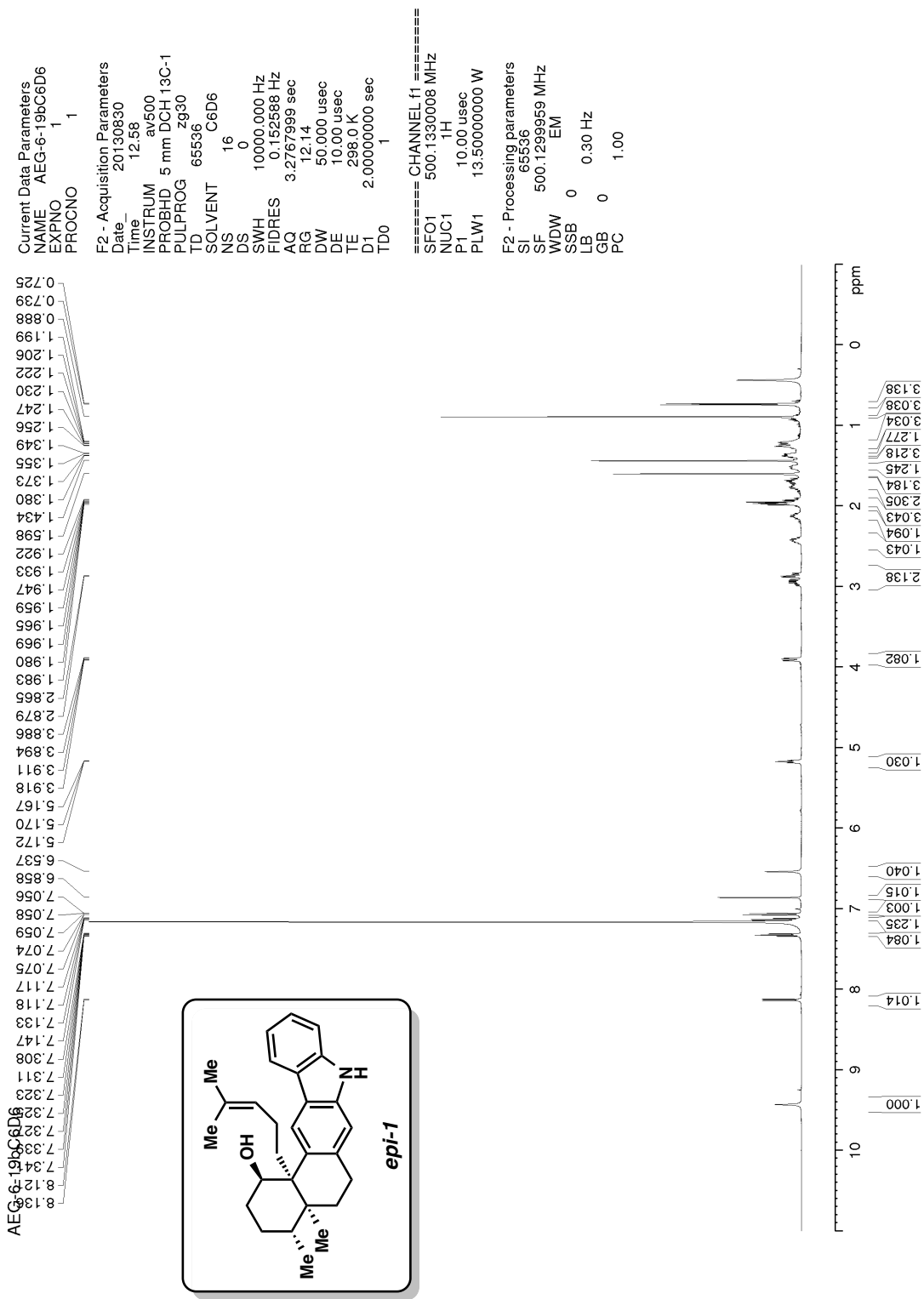
Current Data Parameters
 NAME AEG-6-22aC13
 EXPNO 1
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20130822
 Time_ 11.08
 INSTRUM av500
 PROBHD 5 mm DCH 13C-1
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 40
 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

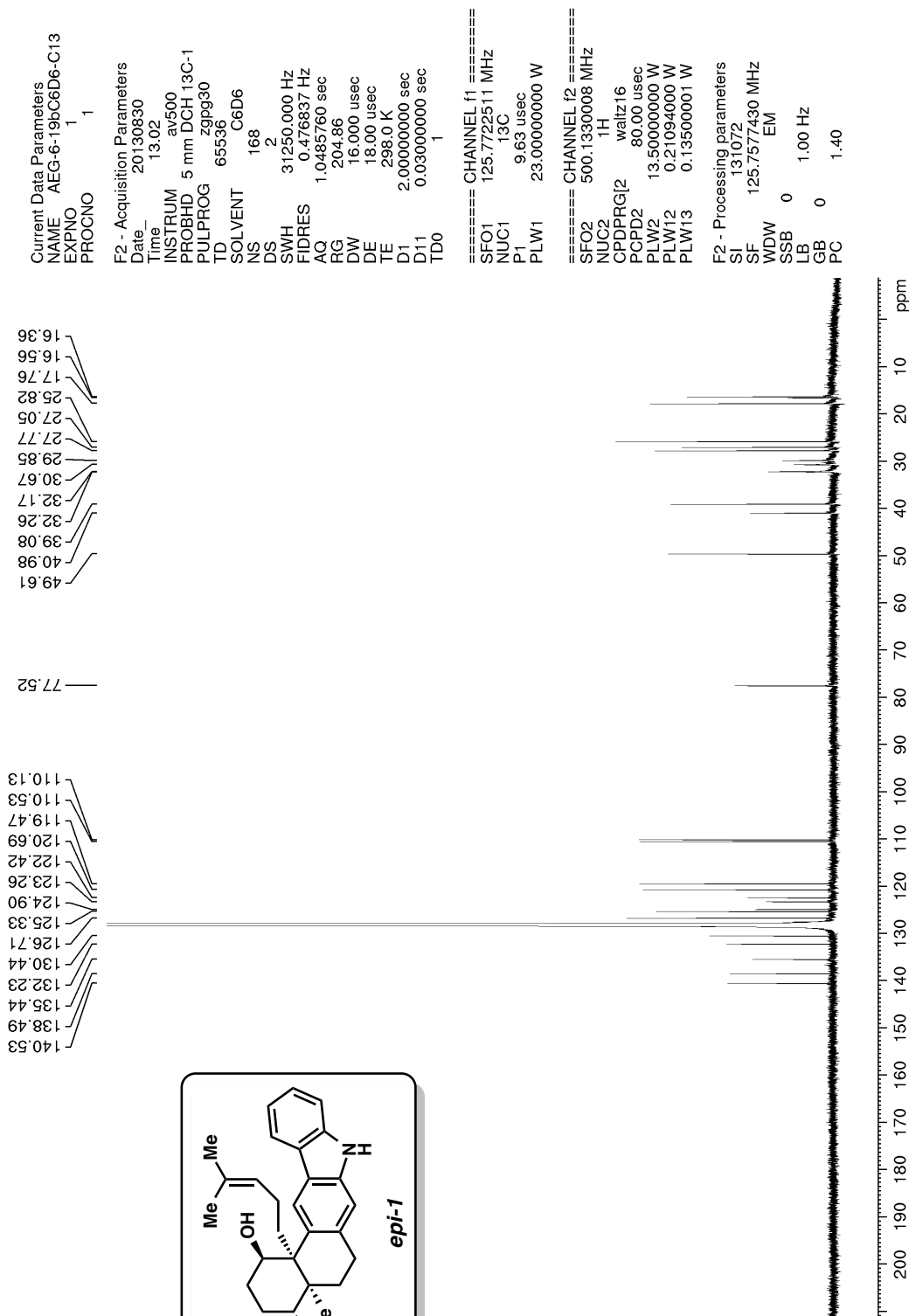
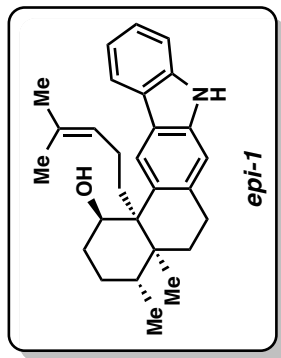
==== CHANNEL f1 =====
 SFO1 125.7722511 MHz
 NUC1 13C
 P1 9.63 usec
 PLW1 23.00000000 W

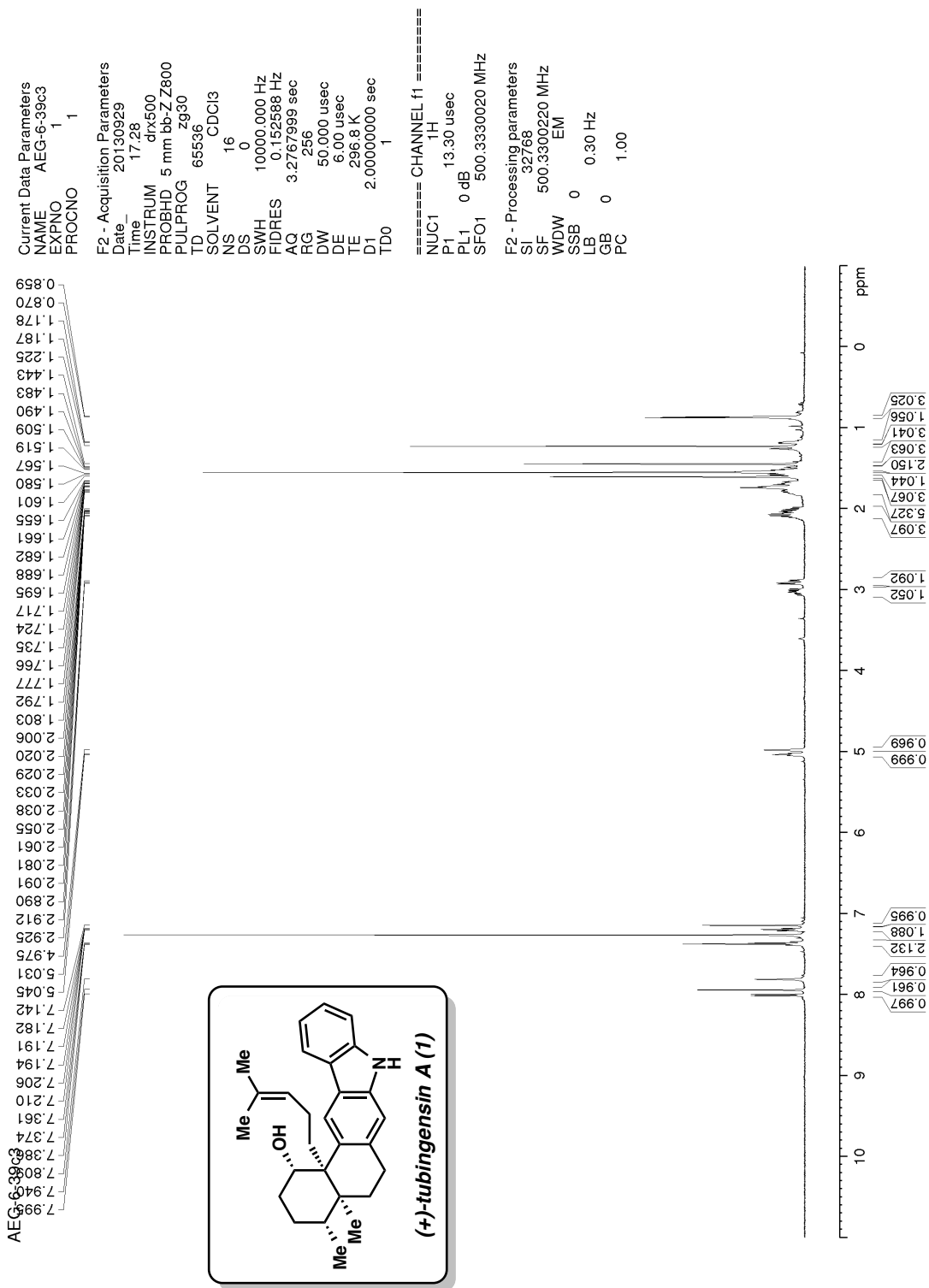
==== CHANNEL f2 =====
 SFO2 500.1330008 MHz
 NUC2 1H
 CPDPRG2 waltz16
 PCPD2 80.00 usec
 PLW2 13.50000000 W
 PLW12 0.21094000 W
 PLW13 0.13500001 W

F2 - Processing parameters
 SI 131072
 SF 125.757733 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

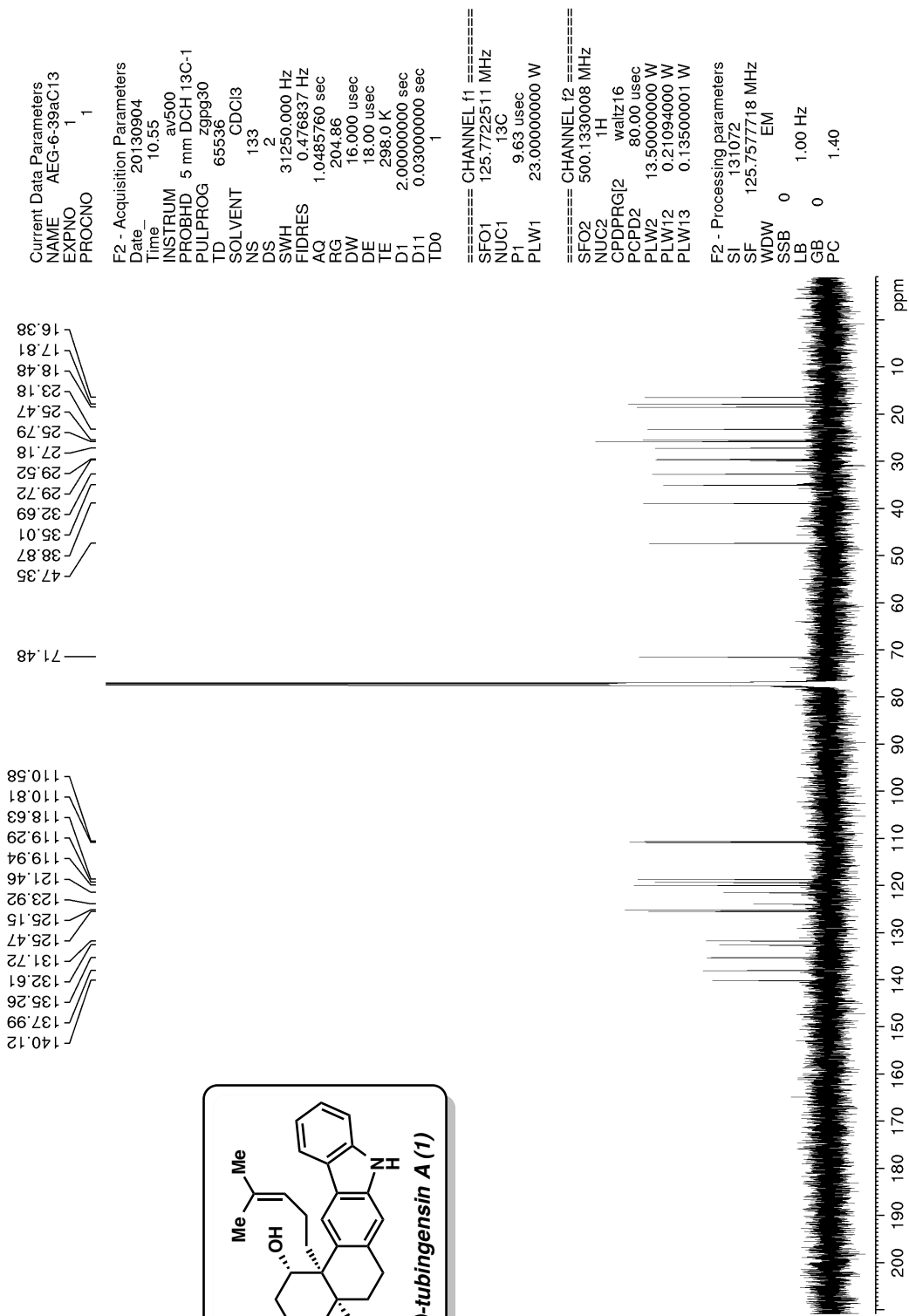
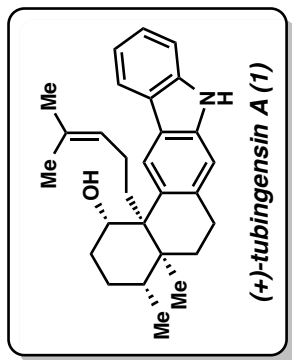


AEG-6-19bC6D6-C13





AEG-6-39aC13



References:

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- ⁵ Lipshutz, B. H.; Ellsworth, E. L.; Dimock, S. H.; Smith, R. A. J. *J. Am. Chem. Soc.* **1990**, *112*, 4404–4410.