

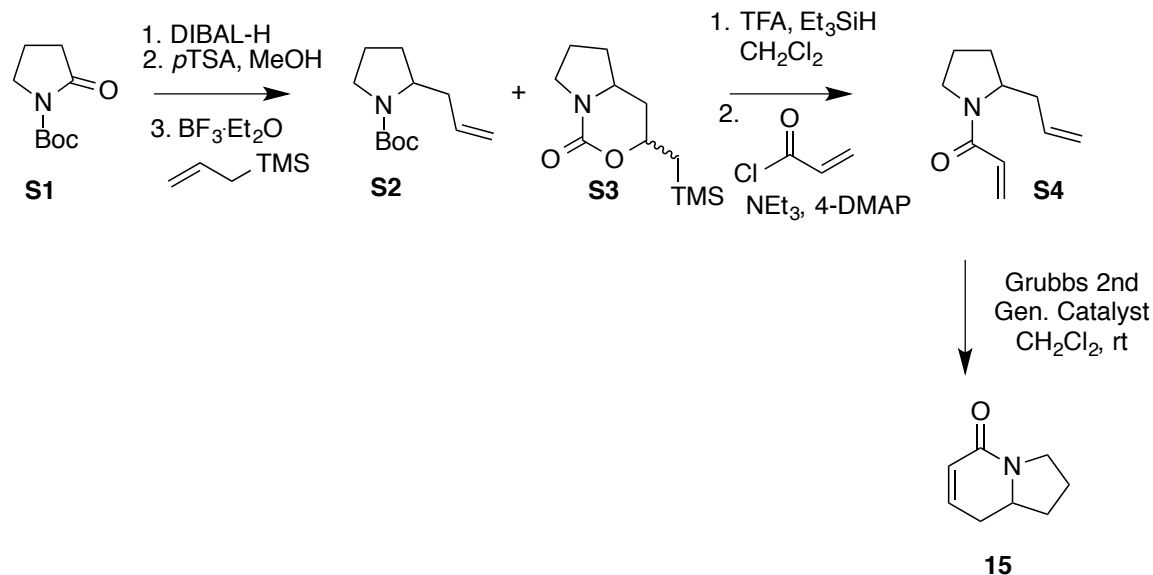
# Total Synthesis of Aspeverin via an Iodine(III)-mediated Oxidative Cyclization

Adam M. Levinson\*

Laboratory for Bioorganic Chemistry  
Sloan-Kettering Institute for Cancer Research  
1275 York Avenue, New York, NY 10065 (USA)

**General Information.** All commercial reagents (Aldrich, Alfa-Aesar, Acros Organics, Fluka) were used without further purification. All solvents were reagent or HPLC grade (Fisher). Anhydrous tetrahydrofuran (THF), diethyl ether (Et<sub>2</sub>O), dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>), toluene (PhMe), and benzene were passed through a column of alumina and used without further drying. All reactions were carried out in flame-dried glassware under an argon or nitrogen atmosphere unless otherwise noted. Analytical TLC was performed on E. Merck silica gel 60 F254 plates and visualized by UV fluorescence quenching and KMnO<sub>4</sub> staining. Preparative thin-layer chromatography (PTLC) separations were performed on E. Merck silica gel 60 F254 plates (1 mm). Flash column chromatography was performed on E. Merck silica gel 60 (40-63 μm). Yields refer to chromatographically and spectroscopically pure compounds. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a Bruker Avance DRX-500 MHz or DRX-600 MHz at ambient temperature unless otherwise stated. Chemical shifts are reported in parts per million relative to residual solvent CDCl<sub>3</sub> (<sup>1</sup>H, 7.26 ppm, <sup>13</sup>C, 77.16 ppm) or DMSO-*d*<sub>6</sub> (<sup>1</sup>H, 2.50 ppm, <sup>13</sup>C, 39.52 ppm). Multiplicities are reported as follows: s = singlet, d = doublet, dd = doublet of doublets, t = triplet, td = triplet of doublets, tt = triplet of triplets, m = multiplet, q = quartet, app. = apparent, br. s = broad singlet. Diastereomeric ratio (dr) was determined by <sup>1</sup>H NMR analysis. High-resolution mass spectral analyses were performed by the MSKCC core facility staff.

**Abbreviations.** DMF = *N,N*-dimethylformamide, DMSO = dimethylsulfoxide, TFA = trifluoroacetic acid, DPPA = diphenylphosphoryl azide, DIBAL-H = diisobutylaluminum hydride, HFIP = 1,1,3,3-hexafluoro-2-propanol, TBS = *tert*-butyldimethylsilyl, Boc = *tert*-butoxycarbonyl, DMAP = 4-dimethylaminopyridine, KHMDS = potassium bis(trimethylsilyl)amide, *p*TSA = *para*-toluenesulfonic acid



### Synthesis of **S2** and **S3**:

To a  $-78^{\circ}\text{C}$  solution of **S1** (46.90 g, 253.2 mmol) in anhydrous  $\text{Et}_2\text{O}$  (135 mL) was added DIBAL-H (1.56 M in anhydrous PhMe, 187 mL, 291 mmol) by cannula over a period of ~30 minutes. The reaction was stirred for 3 hours at  $-78^{\circ}\text{C}$ , then 4 hours at room temperature. The reaction was recooled to  $-78^{\circ}\text{C}$ , and acidic MeOH (350 mg *pTSA* dissolved in 350 mL) was *carefully* added. The resulting mixture was stirred at room temperature overnight and concentrated. Saturated aq. Na/K tartrate (400 mL) was added, and stirred for 3 hours until the mixture became turbid. The aqueous phase was extracted with ether (3 x 250 mL), the combined organic layers washed with brine (300 mL), dried over  $\text{MgSO}_4$  and concentrated. The resulting crude hemiaminal was dissolved in  $\text{CH}_2\text{Cl}_2$  (900 mL) and cooled in an ice bath. Allyltrimethylsilane (65 mL, 409 mmol) was added followed by  $\text{BF}_3\cdot\text{Et}_2\text{O}$  (28 mL, 227 mmol) dropwise over 10 minutes. The reaction was stirred a further 15 minutes at  $0^{\circ}\text{C}$  and 10 minutes at room temperature. 1M aq.  $\text{K}_2\text{CO}_3$  (600 mL) was added, and the organic layer was separated. The aqueous phase was further extracted with  $\text{CH}_2\text{Cl}_2$  (2 x 300 mL), the combined organic layers washed with brine (500 mL), dried over  $\text{MgSO}_4$  and concentrated. Purification by silica gel chromatography (10:1 Hexane/EtOAc  $\rightarrow$  1:1 Hexane/EtOAc  $\rightarrow$  100% EtOAc) afforded **S2** (30.0 g, 142 mmol, 56% yield) as a colorless oil and **S3** (18.29 g, 32% yield, 1.2:1 *dr*) as a low-melting solid. Both **S2** and **S3** react productively in the next steps. **S2** was in spectroscopic agreement as reported in the literature.<sup>1</sup>

### **S3**:

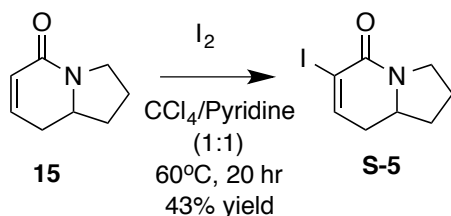
$R_f=0.05$  (silica gel, 2:1 Hexane/EtOAc).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  5.02 – 4.22 (m, 2H), 3.75 – 3.35 (m, 6H), 2.32 – 1.92 (m, 5H), 1.85– 1.69 (m, 3H), 1.54 – 1.27 (m, 4H), 1.27 – 1.10 (m, 2H), 0.95–0.80 (m, 2H), 0.08 (s, 18H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  153.5, 152.9, 76.3, 74.9, 56.8, 52.4, 46.7, 46.5, 36.8, 33.8, 33.5, 33.4, 24.6, 23.1, 23.0, 22.9, -0.7, -0.9. IR (neat):  $\text{cm}^{-1}$  2948, 2894, 1688, 1251, 843. HRMS (ESI, *m/z*) calcd for  $\text{C}_{11}\text{H}_{22}\text{NO}_2\text{Si}$   $[\text{M}+\text{H}]^+$  228.1420, found 228.1411.

### Synthesis of **S4**:

To a 0°C solution of **S2** (23.21 g, 109.8 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (75 mL) was added Et<sub>3</sub>SiH (18 mL, 113 mmol) followed by careful addition of TFA (75 mL, 980 mmol) in small portions. The reaction was stirred for 1.5 hours, and concentrated to yield the corresponding amine TFA salt. The crude salt was then dissolved in CH<sub>2</sub>Cl<sub>2</sub> (211 mL) and cooled to 0°C. NEt<sub>3</sub> (60 mL, 430 mmol) was carefully added followed by 4-dimethylaminopyridine (670 mg, 5.5 mmol). Acryloyl chloride (11.5 mL, 142 mmol) was added dropwise over about 10 minutes, and the reaction was stirred for 2 hours. 1N HCl (200 mL) was then added, and the aqueous phase was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 150 mL). The combined organic layers were washed with brine, dried over MgSO<sub>4</sub> and concentrated. Silica gel chromatography (9:1 Hexane/EtOAc → 1:1 Hexane/EtOAc → 100% EtOAc) afforded **S4** as a light yellow oil (13.51 g, 74% yield over 2 steps), which matched previously reported spectroscopic data.<sup>2</sup>

### Synthesis of 15:

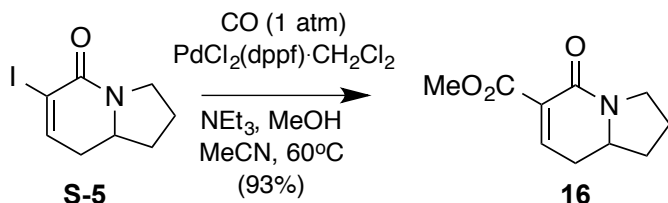
**S4** (11.72 g, 70.9 mmol) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (1.4 L). The reaction was purged by bubbling N<sub>2</sub> through the solution for 20 minutes, at which point Grubbs' 2<sup>nd</sup> Generation catalyst (700 mg, .83 mmol, 1.17 mol%) was added. The reaction was stirred overnight (12 hours) under an atmosphere of N<sub>2</sub> at room temperature and was concentrated. Silica gel chromatography (1:1 CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O → 1:1 CH<sub>2</sub>Cl<sub>2</sub>/EtOAc → 20:1 CH<sub>2</sub>Cl<sub>2</sub>/MeOH) afforded **15** as a light brown oil (9.42 g, 96% yield). **15** matched previously reported spectroscopic data.<sup>2</sup>



### Iodide S-5:

To a solution of **15** (9.42 g, 68.7 mmol) in CCl<sub>4</sub> (335 mL) and pyridine (335 mL) was added solid I<sub>2</sub> (53.0 g, 210 mmol). The resulting mixture was heated at 60°C for 20 hours under an atmosphere of N<sub>2</sub>. The reaction was cooled to room temperature and sat. aq. Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (600 mL) was added followed by 1N HCl (200 mL). The organic layer was separated, and the aqueous phase extracted with EtOAc (3 x 300 mL). The combined organic layers were washed with brine (2 x 350 mL), dried over MgSO<sub>4</sub> and concentrated. Purification by silica gel chromatography (1:1 EtOAc/Hexane → 2:1 EtOAc/Hexane) yielded iodide **S-5** as a white solid (7.76 g, 43% yield). R<sub>f</sub> = 0.59 (silica gel, 1:1 CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O)

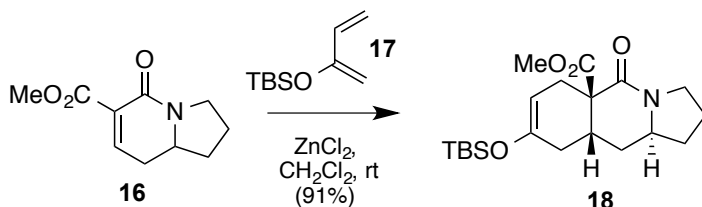
**S-5**: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.18 (dd, *J* = 7.0, 2.3 Hz, 1H), 3.79 (m, 1H), 3.67 (m, 1H), 3.55 (m, 1H), 2.44 (ddd, *J* = 17.1, 6.9, 4.8 Hz, 1H), 2.33 – 2.15 (m, 2H), 2.10 (m, 1H), 1.81 (m, 1H), 1.60 (m, 1H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 159.1, 146.8, 98.2, 56.9, 45.8, 34.2, 33.6, 23.3. IR (neat): cm<sup>-1</sup> 3041, 2969, 2941, 2880, 1649, 1429, 1276. HRMS (ESI, *m/z*) calcd for C<sub>9</sub>H<sub>11</sub>NOI [M+H]<sup>+</sup> 263.9885, found 263.9895.



### Ester 16:

Carbon monoxide gas was bubbled from a balloon through a solution of iodide **S-5** (1.80 g, 7.11 mmol) in MeOH (35 mL) and MeCN (180 mL) for 10 minutes. To the resulting solution was added PdCl<sub>2</sub>(dppf)CH<sub>2</sub>Cl<sub>2</sub> (500 mg, 0.61 mmol) followed by NEt<sub>3</sub> (6.50 mL, 46.6 mmol). Carbon monoxide was then bubbled through the solution for a further 10 minutes, and the mixture was then stirred under a balloon of CO gas at 60°C for 1.5 hr. The reaction mixture was cooled to room temperature under air and concentrated under reduced pressure. The residue was washed with sat. aq. NaHCO<sub>3</sub> (80 mL) and extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 80 mL). The combined organic layers were washed with brine, dried over MgSO<sub>4</sub> and concentrated. Purification by column chromatography (1:1 CH<sub>2</sub>Cl<sub>2</sub>/EtOAc → 15:1 CH<sub>2</sub>Cl<sub>2</sub>/MeOH) yielded ester **16** as a light brown oil that solidifies upon standing (1.28 g, 93%). The product contains a small amount of an adduct resulting from Michael addition of MeOH, which was carried forward in the next step. For characterization purposes, allowing the product mixture to stand briefly in acetic acid fully converted the mixture into **16**. R<sub>f</sub> = 0.20 (silica gel, 1:1 CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O).

**16**: <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.34 (dd, *J* = 6.8, 2.2 Hz, 1H), 3.83 (s, 3H), 3.74 (m, 1H), 3.66 (m, 1H), 3.52 (ddd, *J* = 12.1, 10.1, 7.4 Hz, 1H), 2.61 (m, 1H), 2.35 – 2.19 (m, 2H), 2.04 (m, 1H), 1.82 (m, 1H), 1.67 (m, 1H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 165.2, 159.9, 145.6, 130.6, 56.2, 52.4, 44.7, 33.6, 30.9, 23.4. IR (neat): cm<sup>-1</sup> 2968, 2950, 2884, 1739, 1662, 1613, 1445, 1266. HRMS (ESI, *m/z*) calcd for C<sub>10</sub>H<sub>14</sub>NO<sub>3</sub> [M+H]<sup>+</sup> 196.0974, found 196.0973.



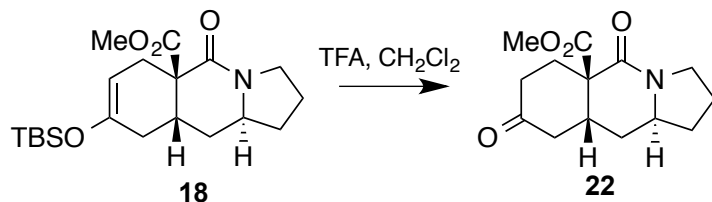
### Diels-Alder Adduct 18:

To a stirred solution of **16** (4.43 g, 22.73 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (225 mL) was added **17** (8.28 g, 45 mmol). Then ZnCl<sub>2</sub> (1M in Diethyl Ether, 23 mL, 23 mmol) was added in one portion and the reaction was stirred for 1.5 hours at room temperature. At this time, more **17** was added (1.14 g, 6.2 mmol) and the reaction stirred a further 30 minutes until all starting material was consumed as determined by TLC analysis. The reaction was quenched by adding sat. aq. NaHCO<sub>3</sub> (250 mL). The layers were separated, and the aqueous layer was further extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 100 mL). The combined organic layers were washed with Brine/sat. NaHCO<sub>3</sub> (1:1, 200 mL), dried over MgSO<sub>4</sub>, and concentrated under reduced pressure. Silica gel chromatography (1:1 EtOAc/Hexanes → 2:1 EtOAc/Hexanes → 100% EtOAc) afforded Diels-Alder adduct **18** (7.88 g, 91%)



yield) as a light orange oil and as a single diastereomer.  $R_f = 0.59$  (silica gel, 1:1  $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ ).

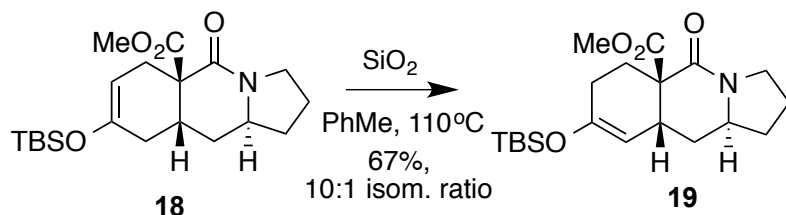
**18**:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  4.84 (m, 1H), 3.77 (m, 1H), 3.73 (s, 3H), 3.59 (m, 1H), 3.30 (ddd,  $J = 12.7, 10.0, 3.0$  Hz, 1H), 2.86 – 2.66 (m, 2H), 2.61 (ddt,  $J = 16.8, 4.2, 2.0$  Hz, 1H), 2.19 (ddd,  $J = 17.7, 6.8, 2.0$  Hz, 1H), 2.13 – 1.88 (m, 4H), 1.76 (m, 2H), 1.50 (m, 1H), 0.89 (s, 9H), 0.09 (s, 6H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  173.5, 168.3, 148.2, 101.3, 55.1, 53.6, 52.7, 44.6, 33.9, 32.9, 31.9, 29.2, 26.8, 25.8, 22.2, 18.1, -4.3, -4.4. IR (neat):  $\text{cm}^{-1}$  2953, 2934, 2892, 2856, 1730, 1647, 1442, 1247, 1178. HRMS (ESI,  $m/z$ ) calcd for  $\text{C}_{20}\text{H}_{34}\text{NO}_4\text{Si}$   $[\text{M}+\text{H}]^+$  380.2257, found 380.2263.



#### Ketone 22:

To a stirred solution of Diels-Alder adduct **18** (62 mg, 0.163 mmol) in  $\text{CH}_2\text{Cl}_2$  (2 mL) was added TFA (50  $\mu\text{L}$ ). The solution was stirred for 5 minutes and quenched with sat. aq.  $\text{NaHCO}_3$  (4 mL).  $\text{CH}_2\text{Cl}_2$  (~8 mL) was added, and the mixture was directly filtered through a phase separator and concentrated. Purification by silica gel chromatography (1:1  $\text{EtOAc}/\text{CH}_2\text{Cl}_2 \rightarrow 10:1 \text{CH}_2\text{Cl}_2/\text{MeOH}$ ) yielded pure ketone **22** as a colorless oil (43 mg, 99% yield).  $R_f = 0.22$  (1:1  $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ )

**22**:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  3.76 (m, 1H), 3.74 (s, 3H), 3.54 (m, 1H), 3.45 (ddd,  $J = 12.4, 9.7, 2.4$  Hz, 1H), 2.75 (m, 1H), 2.54 (m, 1H), 2.50 – 2.28 (m, 5H), 2.10 (m, 2H), 2.05 (m, 1H), 1.90 (m, 2H), 1.84 (m, 1H), 1.52 (m, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  210.5, 173.4, 166.6, 55.0, 53.4, 53.1, 45.4, 42.6, 37.2, 37.1, 33.6, 31.5, 29.4, 22.4. IR (neat):  $\text{cm}^{-1}$  2955, 2887, 1720, 1641, 1269, 1241, 1212. HRMS (ESI,  $m/z$ ) calcd for  $\text{C}_{14}\text{H}_{20}\text{NO}_4$   $[\text{M}+\text{H}]^+$  266.1392, found 266.1380.

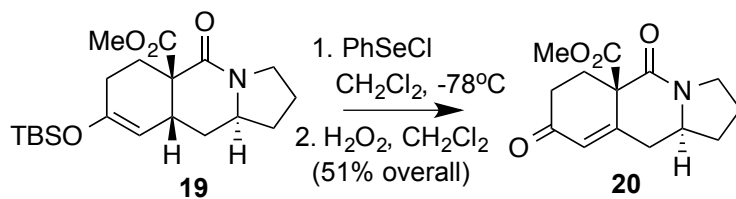


#### Silyl Enol Ether 19:

To a solution of **18** (692 mg, 1.83 mmol) in anhydrous toluene (62 mL) was added silica gel (40-63  $\mu\text{m}$ , oven-dried for 24 hr, 1.89 g). The resulting mixture was stirred vigorously in a sealed vial at  $110^\circ\text{C}$  14 hours, at which point more silica gel (1.30 g) was added, and the mixture stirred a further 24 hours. During the course of the reaction, small aliquots were periodically taken and reaction progress was monitored by  $^1\text{H}$  NMR. The reaction was cooled and filtered to remove silica gel, which was washed with copious amounts of

CH<sub>2</sub>Cl<sub>2</sub>. Purification by silica gel chromatography (1:1 CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O) yielded **19** as a colorless oil (469 mg, 10:1 ratio of product:starting material, 67% yield). R<sub>f</sub> = 0.53 (1:1 CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O)

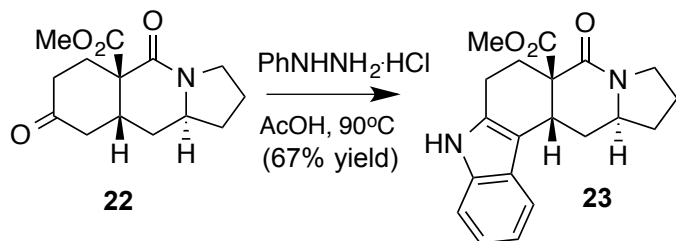
**19**: <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 4.66 (br s, 1H), 3.70 (s, 3H), 3.69 (m, 1H), 3.39 (m, 1H), 2.96 (m, 1H), 2.58 (m, 1H), 2.12 – 1.87 (m, 5H), 1.82 (m, 2H), 1.72 (m, 1H), 1.52 (m, 1H), 0.90 (s, 9H), 0.10 (s, 3H), 0.08 (s, 3H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 174.4, 166.5, 153.0, 105.2, 55.8, 53.0, 52.8, 45.2, 37.1, 33.4, 31.8, 28.4, 26.7, 25.7, 22.5, 18.2, -4.1, -4.2. IR (neat): cm<sup>-1</sup> 2955, 2933, 2891, 2858, 1731, 1641, 1455, 1248, 1176, 840. HRMS (ESI, m/z) calcd for C<sub>20</sub>H<sub>34</sub>NO<sub>4</sub>Si [M+H]<sup>+</sup> 380.2257, found 380.2249.



### Enone **20**:

To a -78°C stirred solution of **19** (469 mg, 1.23 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (22 mL) was added a solution of PhSeCl (345 mg, 1.81 mmol, dissolved in 2.70 mL CH<sub>2</sub>Cl<sub>2</sub>) dropwise over ca. 1 minute. The reaction was stirred for 10 minutes at -78°C, then allowed to stir at room temperature for a further 2 minutes. The reaction was quenched with sat. aq. NaHCO<sub>3</sub> (50 mL), and the aqueous phase was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 40 mL). The combined organic layers were washed with brine, dried over MgSO<sub>4</sub> and concentrated. The crude mixture was quickly filtered through a short column of silica gel (1:1 CH<sub>2</sub>Cl<sub>2</sub>:Et<sub>2</sub>O) to obtain the corresponding crude phenylselenide as a mixture of diastereomers. The resulting crude phenylselenide was immediately dissolved in CH<sub>2</sub>Cl<sub>2</sub> (13 mL), and H<sub>2</sub>O<sub>2</sub> (0.4 mL, 30 wt% in H<sub>2</sub>O) was added. The mixture was stirred for 15 minutes and quenched with sat. aq. NaHCO<sub>3</sub> (20 mL). The aqueous phase was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 20 mL), and the combined organic layers were washed with brine, dried over MgSO<sub>4</sub> and concentrated. Purification by silica gel chromatography (1:1 CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O) yielded pure enone **20** (168 mg, 51% yield overall) as a crystalline white solid. R<sub>f</sub> = 0.35 (silica gel, 1:1 CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O). mp: 114-118°C

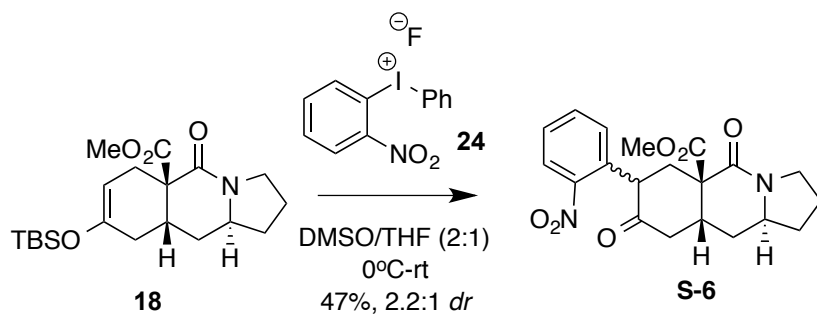
**20**: <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 5.96 (s, 1H), 3.75 (s, 3H), 3.66 (m, 1H), 3.52 (m, 1H), 3.45 (m, 1H), 3.03 (ddd, *J* = 13.8, 5.4, 2.0 Hz, 1H), 2.93 (ddd, *J* = 18.1, 13.8, 5.4 Hz, 1H), 2.83 (ddd, *J* = 12.8, 11.1, 1.7 Hz, 1H), 2.76 (dd, *J* = 12.8, 3.7 Hz, 1H), 2.51 (m, 1H), 2.24 (m, 1H), 2.07 (m, 1H), 1.97 (td, *J* = 13.9, 5.0 Hz, 1H), 1.85 (m, 1H), 1.63 (m, 1H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 198.2, 168.7, 165.5, 156.0, 127.0, 57.7, 53.9, 53.4, 45.9, 38.0, 35.0, 33.8, 30.4, 22.4. IR (neat): cm<sup>-1</sup> 2977, 2958, 2926, 2887, 1739, 1653, 1628, 1441, 1344, 1223, 1166. HRMS (ESI, m/z) calcd for C<sub>14</sub>H<sub>18</sub>NO<sub>4</sub> [M+H]<sup>+</sup> 264.1236, found 264.1246.



### Indole **23**:

To a stirred solution of ketone **22** (111 mg, 0.42 mmol) in AcOH (0.84 mL) was added phenylhydrazine hydrochloride (79 mg, 0.55 mmol). The mixture was heated at 90°C under N<sub>2</sub> for 3 hours, at which point the reaction was concentrated under reduced pressure. Purification by silica gel chromatography (1:1 CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O → 20:1 CH<sub>2</sub>Cl<sub>2</sub>/MeOH) afforded indole **23** as a light orange foam (96 mg, 67% yield). The other potential regioisomer was not observed in the reaction mixture. R<sub>f</sub> = 0.22 (1:1 CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O)

**23**: <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.94 (br s, 1H), 7.51 (d, *J* = 7.9 Hz, 1H), 7.32 (d, *J* = 7.9 Hz, 1H), 7.15 (t, *J* = 7.9 Hz, 1H), 7.08 (t, *J* = 7.9 Hz, 1H), 3.79 (s, 3H), 3.79 (m, 1H), 3.66 (dt, *J* = 12.8, 8.6 Hz, 1H), 3.34 (m, 1H), 2.98 (m, 1H), 2.86 (ddd, *J* = 12.5, 4.3, 2.3 Hz, 1H), 2.81 (dt, *J* = 13.2, 3.5 Hz, 1H), 2.75 – 2.60 (m, 2H), 2.23 (td, *J* = 12.5, 5.9 Hz, 1H), 2.08 (m, 1H), 1.90 (m, 2H), 1.55 (m, 2H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 174.4, 167.0, 136.2, 135.8, 126.4, 121.5, 119.6, 118.6, 111.0, 108.3, 55.3, 55.0, 52.9, 45.5, 36.5, 33.2, 30.3, 29.1, 22.3, 20.3. IR (neat): cm<sup>-1</sup> 3259, 2969m 2952, 2883, 1734, 1674, 1624, 1459, 1330, 1252. HRMS (ESI, *m/z*) calcd for C<sub>20</sub>H<sub>23</sub>N<sub>2</sub>O<sub>3</sub> [M+H]<sup>+</sup> 339.1709, found 339.1715.



### Nitroarene **S-6**:

A stirred solution of Diels-Alder adduct **18** (6.45 g, 17.01 mmol) in DMSO (34 mL) and THF (17 mL) was cooled in an ice bath for 10 minutes, until the mixture became a partially-frozen slurry. To the rapidly stirring mixture was added solid *o*-nitrophenyliodonium fluoride **24** (7.33 g, 21.26 mmol) in one portion.<sup>3</sup> The resulting dark brown mixture was stirred for 2 minutes, at which time the ice bath was removed and the mixture stirred at room temperature for a further 20 minutes. Water (250 mL) was added, and the mixture was extracted with EtOAc (4 x 150 mL). The combined organic layers were washed with brine (100 mL), dried over MgSO<sub>4</sub> and concentrated. Silica gel chromatography (1:1 CH<sub>2</sub>Cl<sub>2</sub>:Et<sub>2</sub>O) afforded a 2.2:1 diastereomeric mixture of nitroarene **S-6** (3.090 g, 47% yield) as a light yellow foam. For characterization purposes, the

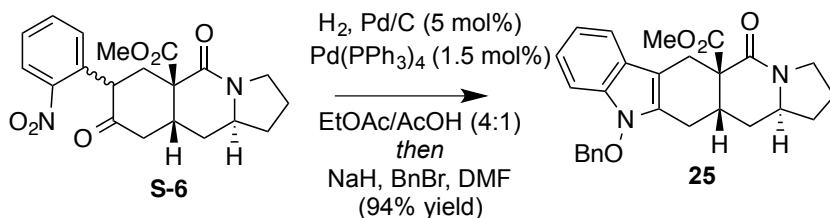
diastereomers can be easily separated by preparative TLC using a 1:1 CH<sub>2</sub>Cl<sub>2</sub>:Et<sub>2</sub>O eluent system.

Nitroarene **S-6**, major diastereomer: R<sub>f</sub> = 0.50 (silica gel, 1:1 CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O)

**S-6**: <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.08 (dd, *J* = 8.3, 1.4 Hz, 1H), 7.62 (td, *J* = 7.6, 1.4 Hz, 1H), 7.45 (ddd, *J* = 8.3, 7.6, 1.4 Hz, 1H), 7.39 (dd, *J* = 7.6, 1.4 Hz, 1H), 4.30 (m, 1H), 3.88 (m, 1H), 3.76 (s, 3H), 3.68 (m, 1H), 3.55 (ddd, *J* = 12.7, 9.9, 2.6 Hz, 1H), 3.26 (dd, *J* = 12.7, 4.7 Hz, 1H), 2.99 (m, 1H), 2.76 (t, *J* = 13.4 Hz, 1H), 2.70 – 2.54 (m, 2H), 2.21 – 2.03 (m, 2H), 2.03 – 1.88 (m, 2H), 1.83 (m, 1H), 1.54 (m, 1H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 206.1, 173.0, 165.4, 149.0, 133.8, 132.9, 129.8, 128.4, 125.6, 55.6, 55.5, 53.4, 49.4, 45.4, 43.0, 39.6, 35.7, 33.5, 30.4, 22.6. IR (neat): cm<sup>-1</sup> 2972, 2953, 2884, 1727, 1639, 1521, 1346, 908. HRMS (ESI, *m/z*) calcd for C<sub>20</sub>H<sub>23</sub>N<sub>2</sub>O<sub>6</sub> [M+H]<sup>+</sup> 387.1556, found 387.1542.

Minor Diastereomer **S-6**: R<sub>f</sub> = 0.43 (silica gel, 1:1 CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O)

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.03 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.61 (td, *J* = 7.6, 1.3 Hz, 1H), 7.52 – 7.37 (m, 2H), 4.32 (br s, 1H), 3.81 (s, 3H), 3.67 (m, 2H), 3.50 (m, 1H), 3.10 – 2.87 (m, 2H), 2.73 (m, 1H), 2.64 (m, 1H), 2.36 (dd, *J* = 15.9, 3.4 Hz, 1H), 2.20 (dt, *J* = 11.9, 5.8 Hz, 1H), 2.12 (m, 1H), 2.09 – 1.97 (m, 2H), 1.87 (m, 1H), 1.61 (m, 1H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 207.67, 173.64, 167.66, 148.34, 134.13, 133.48, 128.66, 125.67, 54.21, 53.22, 52.25, 45.88, 42.58, 34.97, 34.22, 33.90, 31.84, 22.40. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 207.7, 173.7, 167.7, 148.4, 134.1, 133.5, 128.7, 125.7, 54.2, 53.2, 52.2, 45.9, 42.6, 35.0, 34.2, 33.9, 31.8, 22.4. IR (neat): cm<sup>-1</sup> 2953, 2884, 1727, 1635, 1530, 1350, 912. HRMS (ESI, *m/z*) calcd for C<sub>20</sub>H<sub>23</sub>N<sub>2</sub>O<sub>6</sub> [M+H]<sup>+</sup> 387.1556, found 387.1541.

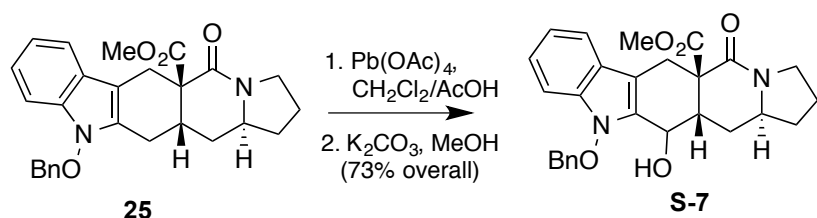


### **N-Benzyloxy Indole 25:**

To a solution of nitroaryl ketone **S-6** (700 mg, 1.81 mmol) in EtOAc (24 mL) and AcOH (6 mL) was added 10% Pd/C (96 mg, 0.090 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (32 mg, 0.028 mmol). H<sub>2</sub> was bubbled from a balloon through the reaction mixture for 10 minutes, and the reaction stirred under 1 atm H<sub>2</sub> for 8.5 hours. The entire reaction contents were concentrated under reduced pressure, and the residue was resuspended in DMF (4.9 mL) and cooled to 0°C. NaH (60% in mineral oil, 250 mg, 6.25 mmol) was then added, and the mixture stirred for 10 minutes. Benzyl bromide (0.35 mL, 2.95 mmol) was then added and the reaction was stirred at room temperature for 45 minutes until all starting material had disappeared by TLC analysis. The mixture was then recooled to 0°C and carefully quenched with sat. aq. NH<sub>4</sub>Cl (30 mL). The aqueous mixture was extracted with EtOAc (4 x 25 mL), the combined organic layers washed with brine (2 x 30 mL), dried over MgSO<sub>4</sub> and concentrated under reduced pressure. Purification by silica gel

chromatography (1:1 CH<sub>2</sub>Cl<sub>2</sub>:Diethyl Ether) afforded alkylated *N*-hydroxyindole **25** as a yellow foam (758 mg, 94% yield). *R*<sub>f</sub> = 0.60 (silica gel, 1:1 CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O).

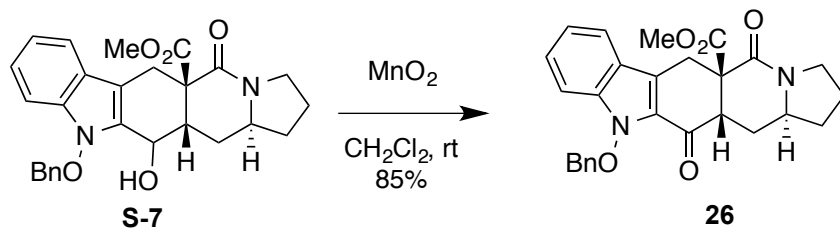
**25**: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.46 (d, *J* = 7.6 Hz, 1H), 7.43 – 7.30 (m, 6H), 7.18 (t, *J* = 7.6 Hz, 1H), 7.10 (t, *J* = 7.6 Hz, 1H), 5.13 (d, *J* = 10.9 Hz, 1H), 5.10 (d, *J* = 10.9 Hz, 1H), 3.76 (m, 1H), 3.71 (s, 3H), 3.55 – 3.43 (m, 3H), 3.32 (ddd, *J* = 12.7, 10.0, 2.9 Hz, 1H), 3.14 (d, *J* = 15.9 Hz, 1H), 2.90 (m, 1H), 2.49 (m, 1H), 2.28 (dd, *J* = 17.2, 4.8 Hz, 1H), 2.14 – 1.86 (m, 3H), 1.86 – 1.68 (m, 2H), 1.52 (m, 1H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 172.8, 168.5, 135.0, 133.8, 130.8, 130.2, 129.2, 128.8, 123.4, 121.9, 119.9, 118.5, 108.3, 103.2, 79.5, 55.0, 54.8, 52.8, 44.6, 34.1, 32.0, 28.7, 23.7, 23.5, 22.1. IR (neat): cm<sup>-1</sup> 3055, 3031, 2952, 2887, 1727, 1638, 1452, 1219, 904. HRMS (ESI, *m/z*) calcd for C<sub>27</sub>H<sub>29</sub>N<sub>2</sub>O<sub>4</sub> [M+H]<sup>+</sup> 445.2127, found 445.2112.



#### Alcohol S-7:

To a room temperature solution of **25** (1.470 g, 3.31 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (18 mL) was added Pb(OAc)<sub>4</sub> (1.830 g, 4.12 mmol) followed by acetic acid (9 mL). The resulting red solution was stirred at room temperature for 30 minutes and concentrated under reduced pressure. The residue was washed with 50 mL sat. aq. NaHCO<sub>3</sub> and extracted into CH<sub>2</sub>Cl<sub>2</sub> (3 x 50 mL). The combined organic layers were washed with brine, dried over MgSO<sub>4</sub>, filtered and concentrated. The crude acetate was then dissolved in anhydrous MeOH (33 mL) and THF (10 mL). K<sub>2</sub>CO<sub>3</sub> (1.830 g, 13.26 mmol) was added and the resulting mixture was stirred vigorously for 6.5 hours, at which point all of the acetate had disappeared by TLC. The mixture was quenched with sat. aq. NH<sub>4</sub>Cl (50 mL), and extracted with EtOAc (4 x 50 mL). The combined organic layers were washed with brine, dried over MgSO<sub>4</sub> and concentrated under reduced pressure. Silica gel chromatography (1:1 CH<sub>2</sub>Cl<sub>2</sub>/Diethyl Ether) afforded alcohol **S-7** as a light yellow foam and as a single unassigned diastereomer. (1.12 g, 73% overall). *R*<sub>f</sub> = 0.34 (silica gel, 1:1 CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O).

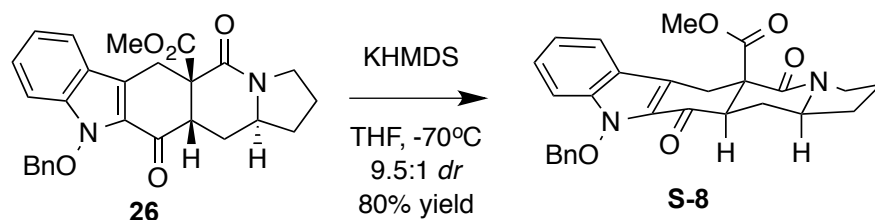
**S-7**: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.52 (d, *J* = 7.9 Hz, 1H), 7.47 – 7.32 (m, 6H), 7.24 (t, *J* = 7.4 Hz, 1H), 7.13 (t, *J* = 7.4 Hz, 1H), 5.33 (d, *J* = 10.4 Hz, 1H), 5.25 (d, *J* = 10.4 Hz, 1H), 4.42 (t, *J* = 5.0 Hz, 1H), 3.87 – 3.76 (m, 1H), 3.73 (s, 3H), 3.58 (d, *J* = 16.2 Hz, 1H), 3.45 (td, *J* = 12.4, 6.4 Hz, 1H), 3.34 (ddd, *J* = 12.4, 10.0, 3.0 Hz, 1H), 3.12 (d, *J* = 16.2 Hz, 1H), 3.02 (ddd, *J* = 10.0, 5.8, 3.8 Hz, 1H), 2.66 (d, *J* = 5.0 Hz, 1H), 2.15 – 1.94 (m, 2H), 1.88 – 1.70 (m, 1H), 1.54 (m, 1H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 173.7, 168.0, 134.9, 134.6, 131.6, 130.1, 129.3, 128.9, 123.3, 122.5, 120.3, 119.6, 108.8, 105.6, 80.0, 64.0, 55.2, 54.1, 52.9, 44.8, 41.0, 33.9, 26.8, 23.9, 22.1. IR (neat): cm<sup>-1</sup> 3368, 2953, 2888, 1723, 1616, 1465, 1320, 1213, 916. HRMS (ESI, *m/z*) calcd for C<sub>27</sub>H<sub>29</sub>N<sub>2</sub>O<sub>5</sub> [M+H]<sup>+</sup> 461.2076, found 461.2064.



### Ketone 26:

Alcohol **S-7** (1.331 g, 2.89 mmol) was dissolved in  $\text{CH}_2\text{Cl}_2$  (120 mL), and activated  $\text{MnO}_2$  (oven-dried for 12 hours, 13.30 g, 153 mmol) was added. The mixture was stirred at room temperature for 18 hours, at which point the reaction contents were filtered through a pad of celite. The filter cake was further washed with  $\text{CH}_2\text{Cl}_2$  (~200 mL), and the filtrate was concentrated to yield ketone **26** (1.130g, 85% yield) as a pale yellow foam, which did not require any additional purification.  $R_f = 0.67$  (1:1  $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ )

**26:**  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.65 (d,  $J = 8.1$  Hz, 1H), 7.56 (m, 2H), 7.48 – 7.36 (m, 3H), 7.33 (ddd,  $J = 8.2, 7.0, 1.1$  Hz, 1H), 7.21 (d,  $J = 8.4$  Hz, 1H), 7.12 (ddd,  $J = 8.1, 7.0, 1.1$  Hz, 1H), 5.34 (d,  $J = 9.6$  Hz, 1H), 5.25 (d,  $J = 9.6$  Hz, 1H), 4.25 (d,  $J = 16.3$  Hz, 1H), 3.83 (s, 3H), 3.67 (dt,  $J = 12.7, 8.8$  Hz, 1H), 3.55 (m, 1H), 3.51 – 3.40 (m, 2H), 3.25 (ddd,  $J = 12.7, 9.8, 2.5$  Hz, 1H), 2.99 (dt,  $J = 13.6, 4.3$  Hz, 1H), 2.10 (m, 1H), 2.03 – 1.89 (m, 1H), 1.86 – 1.64 (m, 2H), 1.46 (m, 1H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  185.1, 172.8, 165.3, 137.7, 134.5, 130.2, 129.3, 128.8, 128.4, 127.4, 124.5, 121.8, 121.5, 120.8, 110.0, 80.8, 57.0, 56.2, 53.4, 48.4, 45.4, 33.4, 27.1, 26.8, 22.4. IR (neat):  $\text{cm}^{-1}$  3036, 3032, 2950, 2880, 1727, 1655, 1445, 1232, 1079. HRMS (ESI,  $m/z$ ) calcd for  $\text{C}_{27}\text{H}_{27}\text{N}_2\text{O}_5$   $[\text{M}+\text{H}]^+$  459.1920, found 459.1904.

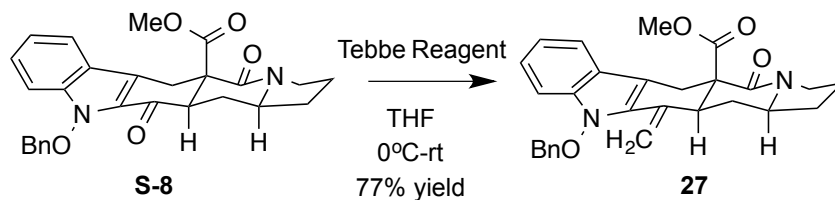


### Trans Ketone S-8:

To a  $-70^\circ\text{C}$  solution of KHMDS (1M in THF, 4.8 mL, 4.8 mmol) was added a solution of ketone **26** (1.130 g, 2.47 mmol) in THF (24 mL) dropwise over 10 minutes. The reaction was stirred for a further 5 minutes, and quenched with sat. aq.  $\text{NH}_4\text{Cl}$  (30 mL). The dry ice/acetone bath was removed, and 20 mL more sat.  $\text{NH}_4\text{Cl}$  was added. The mixture was extracted with EtOAc (4 x 50 mL), the combined organic layers washed with brine (2 x 50 mL), dried over  $\text{MgSO}_4$  and concentrated under reduced pressure. The compound was purified by silica gel chromatography (1:1 Hexane/EtOAc  $\rightarrow$  1:1  $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ ) to afford *trans* ketone **S-8** (907 mg, 80% yield) as a light yellow solid.  $R_f = 0.54$  (1:1  $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ )

**S-8:**  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.64 (d,  $J = 7.8$  Hz, 1H), 7.55 (m, 2H), 7.37 (m, 3H), 7.32 (t,  $J = 7.8$  Hz, 1H), 7.25 (d,  $J = 7.5$  Hz, 1H), 7.14 (t,  $J = 7.5$  Hz, 1H), 5.33 (d,  $J = 9.6$  Hz, 1H), 5.24 (d,  $J = 9.6$  Hz, 1H), 4.24 (d,  $J = 16.6$  Hz, 1H), 3.69 (dt,  $J = 12.6, 8.8$  Hz,

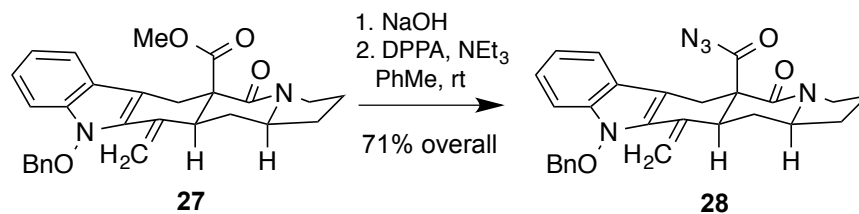
1H), 3.54 (s, 3H), 3.52 (m, 1H), 3.13 (d,  $J = 16.6$  Hz, 1H), 3.03 (dd,  $J = 12.1, 2.6$  Hz, 1H), 2.86 (ddd,  $J = 13.6, 4.4, 2.8$  Hz, 1H), 2.31 – 2.09 (m, 2H), 2.04 (m, 1H), 1.87 (m, 1H), 1.62 (m, 1H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  185.9, 170.3, 164.7, 136.9, 134.5, 130.3, 129.3, 128.7, 127.8, 127.5, 121.8, 121.4, 121.3, 120.8, 110.1, 80.8, 59.5, 57.1, 53.3, 51.9, 45.5, 33.2, 30.9, 25.2, 22.2. IR (neat):  $\text{cm}^{-1}$  3069, 3031, 2973, 2952, 2872, 1724, 1681, 1638, 1438, 1205, 1176. HRMS (ESI,  $m/z$ ) calcd for  $\text{C}_{27}\text{H}_{27}\text{N}_2\text{O}_5$   $[\text{M}+\text{H}]^+$  459.1920, found 459.1908.



### Olefin 27:

To a  $0^\circ\text{C}$  solution of ketone **S-8** (855 mg, 1.86 mmol) in THF (25 mL) was added a solution of Tebbe Reagent (0.5M in PhMe, 13 mL, 6.5 mmol) over a period of about 1 minute. The resulting solution was stirred at room temperature for 30 minutes, recooled to  $0^\circ\text{C}$  and carefully quenched by the slow addition of sat. aq.  $\text{NaHCO}_3$  (60 mL). The mixture was extracted with EtOAc (4 x 50 mL), the combined organic layers washed with brine (2 x 50 mL), dried over  $\text{MgSO}_4$  and concentrated. Purification by silica gel chromatography (1:1  $\text{CH}_2\text{Cl}_2$ :Et $_2\text{O}$ ) yielded olefin **27** as a light yellow foamy solid (657 mg, 77% yield).  $R_f = 0.54$  (1:1  $\text{CH}_2\text{Cl}_2$ /Et $_2\text{O}$ )

**27**:  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.58 (d,  $J = 7.9$  Hz, 1H), 7.47 – 7.34 (m, 7H), 7.26 (t,  $J = 7.9$  Hz, 1H), 7.14 (t,  $J = 7.5$  Hz, 1H), 5.97 (s, 1H), 5.16 (s, 1H), 4.94 (d,  $J = 9.7$  Hz, 1H), 4.90 (d,  $J = 9.7$  Hz, 1H), 4.01 (d,  $J = 16.1$  Hz, 1H), 3.72 (m, 1H), 3.61 (m, 1H), 3.55 (m, 1H), 3.48 (s, 3H), 3.00 (m, 1H), 2.87 (d,  $J = 16.1$  Hz, 1H), 2.54 – 2.31 (m, 2H), 2.23 (m, 1H), 2.06 (m, 1H), 1.87 (m, 1H), 1.70 (m, 1H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  170.7, 166.9, 135.4, 135.3, 134.3, 130.6, 129.7, 129.2, 128.8, 123.8, 123.2, 120.6, 119.7, 110.9, 109.2, 107.8, 78.3, 59.1, 55.4, 52.6, 45.6, 44.9, 33.6, 29.9, 27.2, 22.4. IR (neat):  $\text{cm}^{-1}$  3066, 3031, 2973, 2955, 2883, 1728, 1680, 1638, 1330, 1205, 735. HRMS (ESI,  $m/z$ ) calcd for  $\text{C}_{28}\text{H}_{29}\text{N}_2\text{O}_4$   $[\text{M}+\text{H}]^+$  457.2127, found 457.2107.

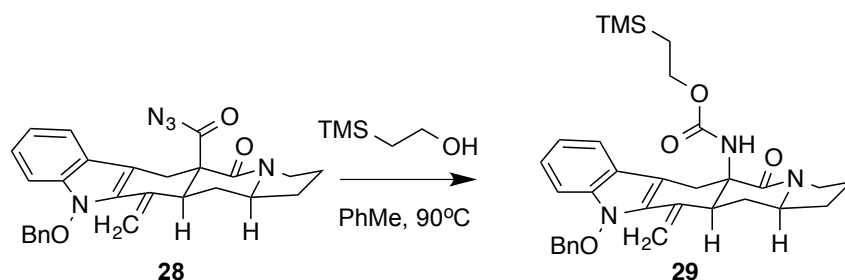


### Acyl azide 28:

Ester **27** (500 mg, 1.09 mmol) was dissolved in 1,4-Dioxane (10 mL) and MeOH (10 mL). To the resulting solution was added aq.  $\text{NaOH}$  (820 mg dissolved in 1.25 mL  $\text{H}_2\text{O}$ ), and the mixture was heated at  $55^\circ\text{C}$  for 18 hours. The reaction mixture was cooled to room temperature and quenched by the addition of 0.5M  $\text{HCl}$  (75 mL). The mixture was

extracted with EtOAc (4 x 50 mL), the combined organic layers washed with brine (2 x 50 mL), dried over MgSO<sub>4</sub> and concentrated. The crude carboxylic acid was immediately resuspended in anhydrous toluene (11 mL), and NEt<sub>3</sub> (0.95 mL) and diphenylphosphoryl azide (0.95 mL) were added. The mixture was stirred for 45 minutes at room temperature, and the entire reaction contents were loaded onto a column of silica gel and purified (1:1 EtOAc/Hexanes → 2:1 EtOAc/Hexanes) to yield acyl azide **28** as a colorless foam (362 mg, 71% yield overall). R<sub>f</sub> = 0.70 (silica gel, 1:1 CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O).

**28:** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.58 (d, *J* = 7.8 Hz, 1H), 7.40 (m, 6H), 7.29 (d, *J* = 7.2 Hz, 1H), 7.16 (t, *J* = 7.8 Hz, 1H), 6.03 (s, 1H), 5.22 (s, 1H), 4.98 (d, *J* = 9.7 Hz, 1H), 4.93 (d, *J* = 9.7 Hz, 1H), 3.98 (d, *J* = 16.5 Hz, 1H), 3.71 (m, 1H), 3.64 – 3.48 (m, 2H), 2.99 (dd, *J* = 11.8, 3.0 Hz, 1H), 2.90 (d, *J* = 16.5 Hz, 1H), 2.58 – 2.36 (m, 2H), 2.24 (m, 1H), 2.09 (m, 1H), 1.90 (m, 1H), 1.72 (m, 1H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 178.3, 165.9, 135.2, 134.6, 134.1, 130.5, 129.6, 129.2, 128.8, 124.0, 122.9, 120.7, 119.6, 110.0, 109.1, 108.4, 78.4, 59.1, 56.3, 45.7, 44.9, 33.4, 30.0, 27.0, 22.3. IR (neat): cm<sup>-1</sup> 3062, 3037, 2973, 2943, 2891, 2128, 1716, 1628, 1173. HRMS (ESI, *m/z*) calcd for C<sub>27</sub>H<sub>26</sub>N<sub>5</sub>O<sub>3</sub> [M+H]<sup>+</sup> 468.2036, found 468.2029.

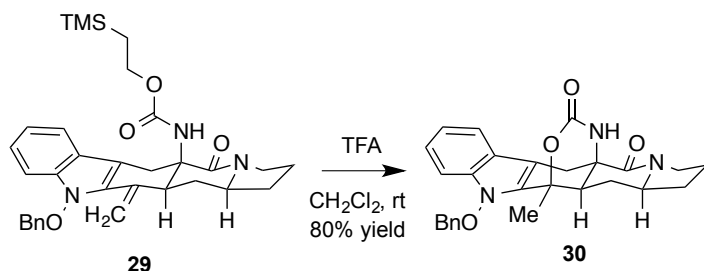


#### Carbamate **29**:

Acyl azide **28** (362 mg, 0.77 mmol) was dissolved in anhydrous toluene (5.6 mL) and heated to 90°C for 20 minutes under a nitrogen atmosphere (N<sub>2</sub> starts visibly bubbling from reaction mixture within about 1 minute of heating at 90°C). To the resulting formed isocyanate was added 2-(trimethylsilyl)ethanol (1.4 mL) and the reaction mixture was heated at 90°C for 9 hours, at which point the entire reaction contents were loaded onto a column of silica gel and purified (2:1 Hexanes/Acetone → 1:1 Hexanes/Acetone) to yield carbamate **29** as a light yellow foamy solid (285 mg, 66% yield). R<sub>f</sub> = 0.62 (silica gel, 1:1 CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O)

**29:** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.51 (d, *J* = 7.8 Hz, 1H), 7.48 – 7.36 (m, 6H), 7.29 (t, *J* = 7.6 Hz, 1H), 7.15 (t, *J* = 7.8 Hz, 1H), 6.13 (s, 1H), 5.26 (s, 1H), 5.05 (d, *J* = 9.6 Hz, 1H), 4.98 (d, *J* = 9.6 Hz, 1H), 4.86 (s, 1H), 3.98 (m, 2H), 3.84 (m, 1H), 3.75 – 3.57 (m, 1H), 3.52 (m, 2H), 3.07 (d, *J* = 16.5 Hz, 1H), 2.94 (m, 1H), 2.26 (m, 1H), 2.19 – 1.98 (m, 2H), 1.82 (m, 1H), 0.82 (m, 2H), -0.05 (s, 9H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 167.87, 155.93, 134.98, 134.62, 134.01, 130.24, 129.75, 129.35, 128.86, 124.05, 123.14, 120.82, 119.33, 110.16, 109.07, 106.39, 78.85, 63.10, 59.69, 57.63, 47.23, 45.70, 34.48, 32.76, 25.73, 22.92, 17.47, -1.37. IR (neat): cm<sup>-1</sup> 3431, 3062, 2952, 2893, 1724, 1641, 1330, 1247, 1226. HRMS (ESI, *m/z*) calcd for C<sub>32</sub>H<sub>40</sub>N<sub>3</sub>O<sub>4</sub>Si [M+H]<sup>+</sup> 558.2788, found 558.2787.

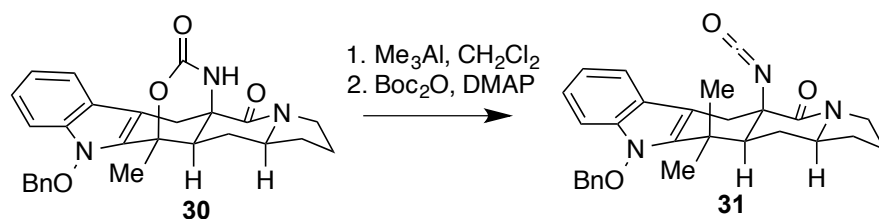




### Cyclic Carbamate **30**:

To a room temperature solution of carbamate **29** (200 mg, 0.34 mmol) in  $\text{CH}_2\text{Cl}_2$  (18 mL) was added TFA (50  $\mu\text{L}$ , 0.65 mmol), and the mixture was stirred for 30 minutes, whereupon more TFA (50  $\mu\text{L}$ , 0.65 mmol) was added. After stirring for an additional 45 minutes, sat. aq.  $\text{NaHCO}_3$  (20 mL) was added. The aqueous phase was further extracted with  $\text{CH}_2\text{Cl}_2$  (3 x 30 mL), the combined organic layers washed with brine, dried over  $\text{MgSO}_4$  and concentrated. Purification by silica gel chromatography (1:1  $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$   $\rightarrow$  1:1:0.1  $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}/\text{MeOH}$ ) afforded bicyclic carbamate **30** as a white crystalline solid (124 mg, 80% yield). m.p.: 220-230°C (decomp.)  $R_f$  = 0.22 (1:1  $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ ).

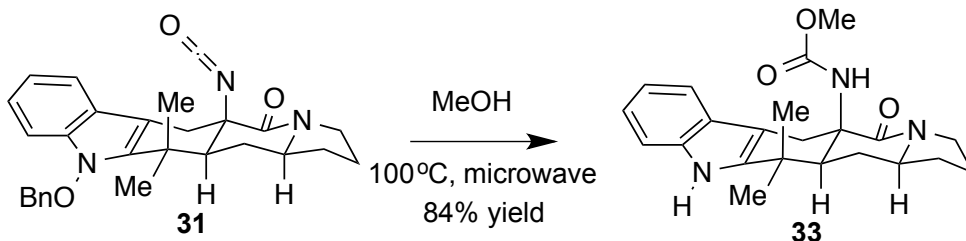
**30**:  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.56 (m, 2H), 7.52 (d,  $J$  = 7.8 Hz, 1H), 7.48 – 7.39 (m, 4H), 7.30 (t,  $J$  = 7.8 Hz, 1H), 7.16 (t,  $J$  = 7.4 Hz, 1H), 5.48 (s, 1H), 5.22 (d,  $J$  = 9.4 Hz, 1H), 5.08 (d,  $J$  = 9.4 Hz, 1H), 3.67 (m, 1H), 3.63 – 3.45 (m, 3H), 2.85 (d,  $J$  = 16.3 Hz, 1H), 2.46 (m, 1H), 2.34 (m, 1H), 2.26 (m, 1H), 2.10 (m, 4H), 1.88 (m, 1H), 1.61 (m, 1H), 1.49 (m, 1H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  167.7, 152.4, 134.7, 134.2, 130.7, 130.0, 129.3, 128.9, 124.4, 122.2, 121.0, 119.5, 109.6, 107.5, 80.2, 75.5, 58.5, 56.8, 45.7, 43.1, 33.8, 33.6, 25.3, 22.6, 20.2. IR (neat):  $\text{cm}^{-1}$  3242, 3054, 2962, 2887, 1702, 1638, 1344, 1068. HRMS (ESI,  $m/z$ ) calcd for  $\text{C}_{27}\text{H}_{28}\text{N}_3\text{O}_4$   $[\text{M}+\text{H}]^+$  458.2065, found 458.2080.



### Isocyanate **31**:

To a 0°C solution of **30** (145 mg, 0.317 mmol) in  $\text{CH}_2\text{Cl}_2$  (11.5 mL) was added  $\text{Me}_3\text{Al}$  dropwise (2M solution in toluene, 2.90 mL, 5.80 mmol). The reaction was stirred for 1.5 hours at 0°C, and was carefully quenched with sat. aq.  $\text{NaHCO}_3$  (30 mL). The mixture was extracted with  $\text{EtOAc}$  (4 x 40 mL), the combined organic layers washed with brine, dried over  $\text{MgSO}_4$  and concentrated. The crude amine was then redissolved in  $\text{CH}_2\text{Cl}_2$  (3 mL), and 4-dimethylaminopyridine (48 mg, 0.39 mmol) was added followed by  $\text{Boc}_2\text{O}$  (0.10 mL, 0.43 mmol). The reaction was stirred for 1 hour, and loaded directly onto preparative TLC plates (100% Hexanes then 1:1  $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ ) to yield isocyanate **31** (49 mg, 34% yield) as an amorphous white solid.  $R_f$  = 0.80 (silica gel, 1:1  $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ )

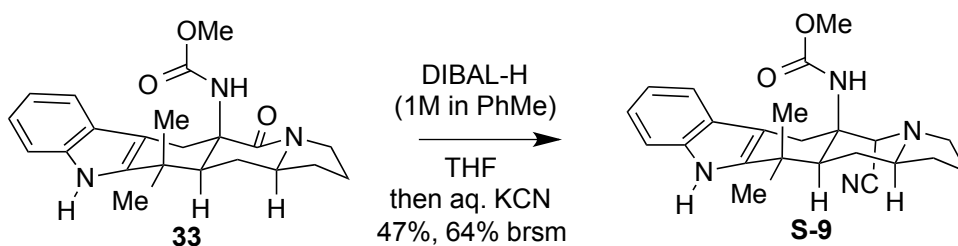
**31:**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.65 – 7.41 (m, 6H), 7.25 (d,  $J = 7.4$  Hz, 3H), 7.14 (t,  $J = 7.4$  Hz, 1H), 5.33 (d,  $J = 10.1$  Hz, 1H), 5.23 (d,  $J = 10.1$  Hz, 1H), 3.78 (dt,  $J = 12.2, 8.9$  Hz, 1H), 3.62 (d,  $J = 16.1$  Hz, 1H), 3.52 – 3.31 (m, 2H), 2.92 (d,  $J = 16.1$  Hz, 1H), 2.28 – 2.14 (m, 2H), 2.07 (m, 1H), 1.92 (dd,  $J = 12.3, 1.8$  Hz, 1H), 1.89 – 1.80 (m, 1H), 1.60 (m,  $J = 4.1$  Hz, 1H), 1.55 (s, 3H), 1.54 (s, 3H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  168.3, 137.9, 134.6, 133.8, 129.1, 129.0, 128.8, 126.8, 123.4, 122.4, 120.2, 118.8, 108.7, 102.3, 78.6, 61.8, 59.9, 49.5, 45.5, 35.6, 34.2, 33.5, 28.6, 26.1, 22.4, 21.4. IR (neat):  $\text{cm}^{-1}$  2969, 2894, 2234 (sharp), 1649, 1452. HRMS (ESI,  $m/z$ ) calcd for  $\text{C}_{28}\text{H}_{30}\text{N}_3\text{O}_3$   $[\text{M}+\text{H}]^+$  456.2287, found 456.2280.



### Carbamate **33**:

Isocyanate **31** (61 mg, 0.13 mmol) was suspended in 5 mL anhydrous MeOH and heated in a Biotage microwave reactor (closed system) at  $100^\circ\text{C}$  for 13 hours (the isocyanate is completely hydrolyzed within minutes by TLC analysis, but reduction to the free indole requires several hours). The resulting solution was concentrated and purified by preparative TLC (1:1  $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ ) to yield carbamate **33** as an amorphous white solid (43 mg, 84%).  $R_f = 0.26$  (1:1  $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ )

**33:**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.15 (s, 1H), 7.48 (d,  $J = 7.6$  Hz, 1H), 7.35 (d,  $J = 7.6$  Hz, 1H), 7.18 (t,  $J = 7.6$  Hz, 1H), 7.12 (t,  $J = 7.6$  Hz, 1H), 4.92 (s, 1H), 3.95 – 3.78 (m, 1H), 3.61 – 3.34 (m, 6H), 2.92 (d,  $J = 15.8$  Hz, 1H), 2.25 – 1.99 (m, 6H), 1.97 – 1.70 (m, 2H), 1.40 (s, 3H), 1.34 (s, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  168.8, 156.2, 141.1, 136.6, 127.7, 122.0, 119.8, 118.5, 110.9, 104.2, 60.5, 57.4, 52.1, 50.3, 45.7, 34.8, 34.3, 32.7, 30.3, 24.7, 22.9. IR (neat):  $\text{cm}^{-1}$  3424, 3266, 2969, 2869, 1724, 1634, 1502, 1455, 1244, 911. HRMS (ESI,  $m/z$ ) calcd for  $\text{C}_{22}\text{H}_{27}\text{N}_3\text{O}_3$   $[\text{M}+\text{H}]^+$  382.2131, found 382.2137.

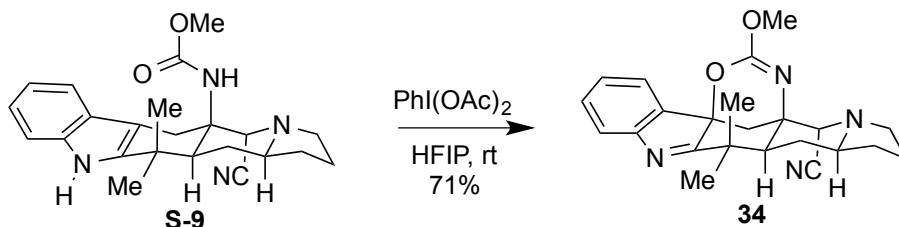


### $\alpha$ -Cyanoamine **S-9**

In a flame-dried 25mL round bottom flask was dissolved lactam **33** (43 mg, 0.11 mmol) in THF (1.14 mL). The solution was cooled to  $-45^\circ\text{C}$  in an acetone/dry ice bath, and DIBAL-H (1M in PhMe, 1.0 mL, 1.0 mmol) was added dropwise over 1 minute. The

reaction was then stirred for 2 hours, maintaining the reaction bath temperature between  $-40^{\circ}\text{C}$  and  $-30^{\circ}\text{C}$  the entire time by periodically adding more dry ice. The reaction was then allowed to warm to  $-15^{\circ}\text{C}$  over 20 minutes, and was quenched with an aqueous solution of KCN (375 mg dissolved in 1.18 mL  $\text{H}_2\text{O}$ ). The mixture was stirred for 45 minutes vigorously at room temperature, at which point sat. aq. Na/K tartrate (8 mL) and sat.  $\text{NaHCO}_3$  (2 mL) were added and stirred vigorously until the reaction mixture became turbid. The mixture was further diluted with 8 mL sat. aq. Na/K tartrate and extracted with EtOAc (3 x 20 mL), the combined organic layers were washed with brine (15 mL), dried over  $\text{MgSO}_4$  and concentrated. Purification by preparative TLC (1:1 Hexane/EtOAc) afforded **S-9** as an amorphous white solid and as a single diastereomer (21 mg, 47% yield). Further elution of the preparative TLC plate (1:1  $\text{CH}_2\text{Cl}_2/\text{EtOAc}$ ) afforded recovered starting material (7.5 mg, 17% yield, 64% brsm).  $R_f = 0.53$  (silica gel, 1:1 Hexane/EtOAc).

**S-9**:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.79 (br s, 1H), 7.51 (d,  $J = 7.8$  Hz, 1H), 7.31 (d,  $J = 7.8$  Hz, 1H), 7.15 (t,  $J = 7.4$  Hz, 1H), 7.10 (t,  $J = 7.4$  Hz, 1H), 5.06 (s, 1H), 4.78 (s, 1H), 4.03 (d,  $J = 16.0$  Hz, 1H), 3.51 (s, 3H), 3.04 (d,  $J = 16.0$  Hz, 1H), 3.00 (dt,  $J = 8.6, 2.7$  Hz, 1H), 2.54 (m, 2H), 2.09 (dd,  $J = 13.0, 3.5$  Hz, 1H), 2.01 (m, 2H), 1.89 (m, 1H), 1.81 (m, 1H), 1.52 (m, 1H), 1.39 (s, 3H), 1.32 (s, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  155.2, 139.0, 136.4, 127.6, 121.9, 119.6, 118.7, 115.9, 110.6, 105.1, 58.4, 58.2, 56.4, 51.9, 50.9, 46.6, 34.0, 30.7, 30.5, 27.4, 24.9, 21.3. IR (neat):  $\text{cm}^{-1}$  3370, 2962, 2880, 2822, 1713, 1512, 1463, 1241, 907. HRMS (ESI,  $m/z$ ) calcd for  $\text{C}_{23}\text{H}_{28}\text{N}_4\text{O}_5$   $[\text{M}+\text{H}]^+$  393.2291, found 393.2300.



#### Compound 34:

To a room temperature solution of **S-9** (21.0 mg, 0.053 mmol) in 1,1,3,3-hexafluoro-2-propanol (2 mL) was added  $\text{PhI(OAc)}_2$  (23 mg, 0.071 mmol), and the mixture was allowed to stand for 8 minutes. The reaction mixture was concentrated under reduced pressure and purified by preparative TLC (1:1 Hexane/EtOAc) to yield **34** (15.0 mg, 71% yield) as a colorless oil.  $R_f = 0.50$  (silica gel, 1:1 Hexane/EtOAc).

**34**:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.57 (d,  $J = 7.7$  Hz, 1H), 7.43 (t,  $J = 7.7$  Hz, 1H), 7.39 (d,  $J = 7.4$  Hz, 1H), 7.26 (t,  $J = 7.4$  Hz, 1H), 3.83 (s, 1H), 3.80 (s, 3H), 3.05 (td,  $J = 8.6, 2.9$  Hz, 1H), 2.54 (q,  $J = 8.6$  Hz, 1H), 2.42 (m, 1H), 2.19 (d,  $J = 13.4$  Hz, 1H), 2.04 – 1.94 (m, 2H), 1.91 (d,  $J = 13.4$  Hz, 1H), 1.90 – 1.73 (m, 3H), 1.68 (m, 1H), 1.59 (m, 1H), 1.45 (s, 3H), 1.09 (s, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  186.2, 153.4, 152.8, 135.6, 131.0, 126.7, 123.0, 121.3, 115.3, 86.0, 63.4, 59.3, 55.9, 55.6, 51.7, 50.8, 39.9, 38.3, 30.3, 27.5, 27.4, 21.5, 21.4. IR (neat):  $\text{cm}^{-1}$  2969, 2955, 2869, 2819, 1674, 1580, 1308, 1262, 904. HRMS (ESI,  $m/z$ ) calcd for  $\text{C}_{23}\text{H}_{26}\text{N}_4\text{O}_2$   $[\text{M}+\text{H}]^+$  391.2134, found 391.2146.

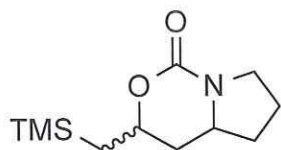




NMR Analytical Core Facility  
Ckefeller Research Laboratories  
430 E 67th St  
New York, NY 10021

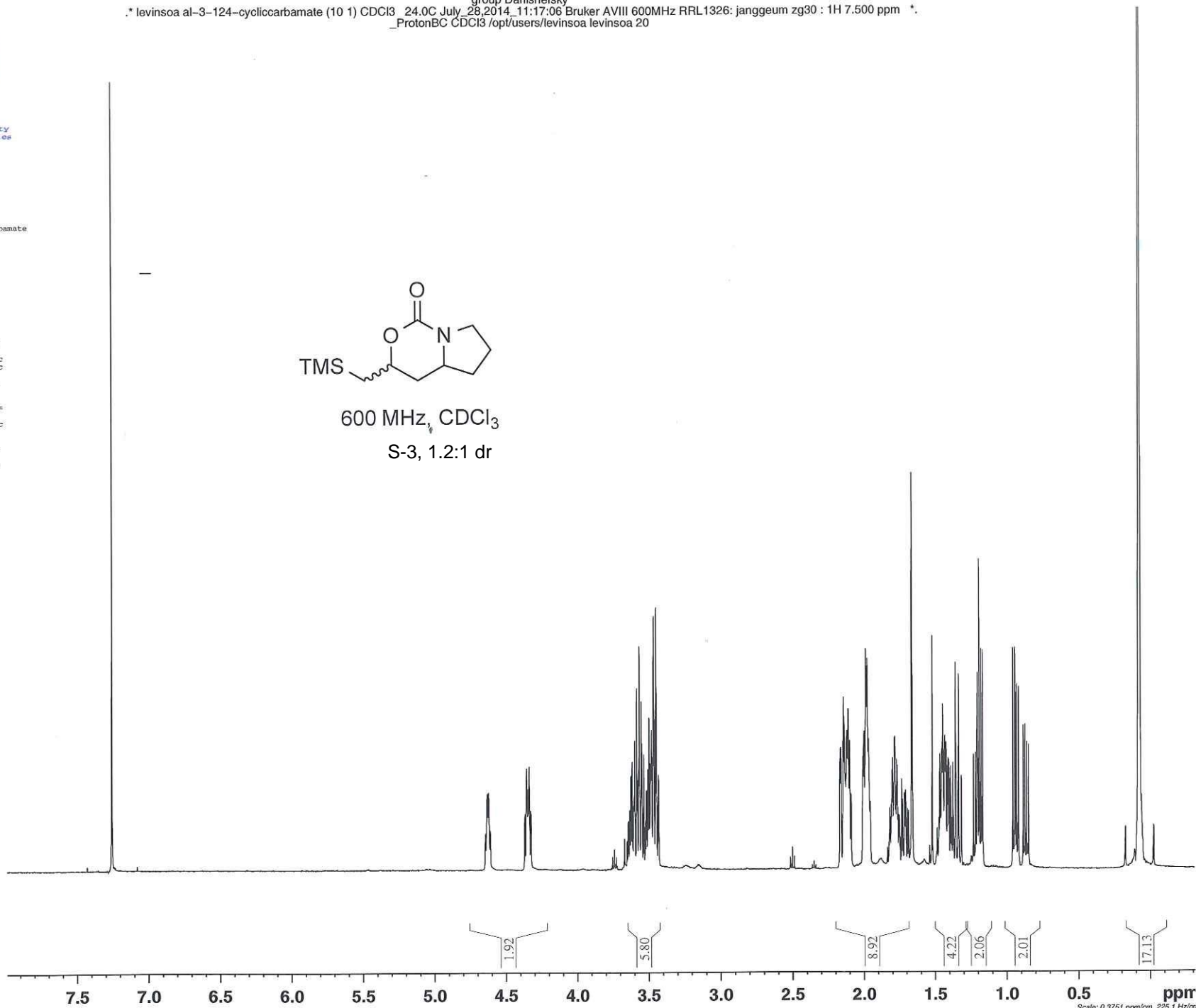
group Danishefsky  
\* levinsoa al-3-124-cycliccarbamate (10 1) CDCl3 24.0C July 28, 2014\_11:17:06 Bruker AVIII 600MHz RRL1326: janggeum zg30 : 1H 7.500 ppm  
\_ProtonBC CDCl3 /opt/users/levinsoa levinsoa 20

NAME al-3-124-cycliccarbamate  
EXPNO 10  
PROCNO 1  
Date\_ 20140728  
Time\_ 11.18  
INSTRUM spect  
PROBHD 5 mm PATXO 19P  
PULPROG zg30  
TD 65536  
SOLVENT CDCl3  
NS 24  
DS 0  
SWH 13227.514 Hz  
FIDRES 0.201836 Hz  
AQ 2.4773109 sec  
RG 256  
DW 37.800 usec  
DE 9.23 usec  
TE 297.2 K  
D1 1.00000000 sec  
TD0 1

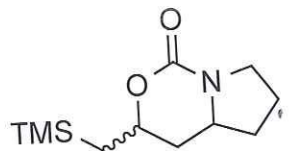


600 MHz, CDCl<sub>3</sub>  
S-3, 1.2:1 dr

===== CHANNEL f1 =====  
NUC1 1H  
P1 12.90 usec  
PL1 -1.30 dB  
PL1W 27.78522110 W  
SFO1 600.1345010 MHz  
S1 65536  
SF 600.1300186 MHz  
WDW EM  
SSB 0  
LB 0.31 Hz  
GB 0  
PC 1.00



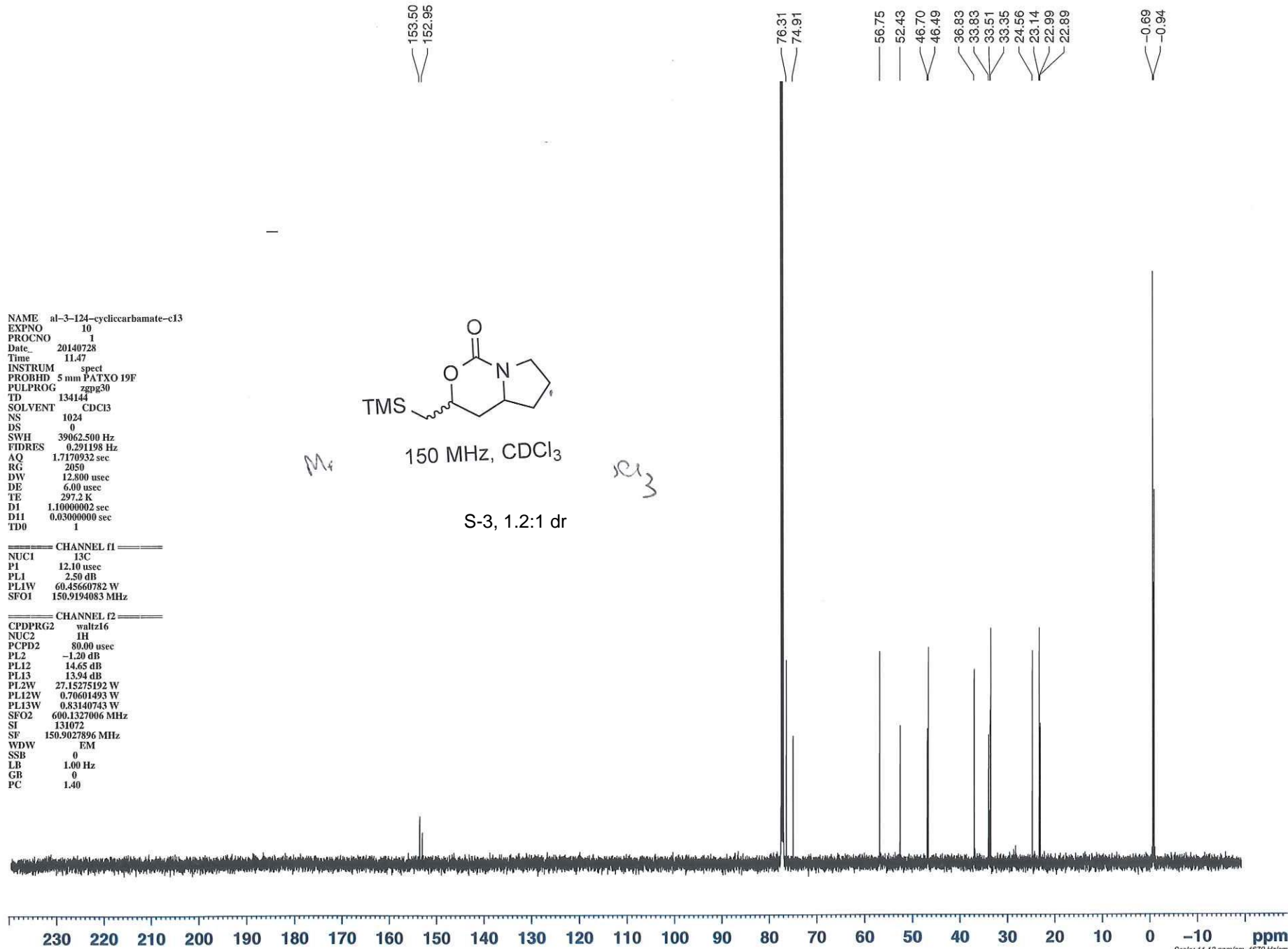
NAME al-3-124-cycliccarbamate-c13  
 EXPNO 10  
 PROCNO 1  
 Date\_ 20140728  
 Time 11.47  
 INSTRUM spect  
 PROBHD 5 mm PATXO 19F  
 PULPROG zgpg30  
 TD 134144  
 SOLVENT CDCl3  
 NS 1024  
 DS 0  
 SWH 39062.500 Hz  
 FIDRES 0.291198 Hz  
 AQ 1.7170932 sec  
 RG 2050  
 DW 12.800 usec  
 DE 6.00 usec  
 TE 297.2 K  
 DI 1.10000002 sec  
 D11 0.03000000 sec  
 TD0 1



150 MHz, CDCl<sub>3</sub>

S-3, 1.2:1 dr

==== CHANNEL f1 =====  
 NUC1 13C  
 P1 12.10 usec  
 PL1 2.50 dB  
 PL1W 60.45660782 W  
 SFO1 150.9194083 MHz  
 ===== CHANNEL f2 =====  
 CPDPRG2 waltz16  
 NUC2 1H  
 PCPD2 80.00 usec  
 PL2 -1.20 dB  
 PL12 14.65 dB  
 PL13 13.94 dB  
 PL2W 27.15275192 W  
 PL12W 0.70601493 W  
 PL13W 0.83140743 W  
 SFO2 600.1327006 MHz  
 SI 131072  
 SF 150.9027896 MHz  
 WDW EM  
 SSB 0  
 LB 1.00 Hz  
 GB 0  
 PC 1.40





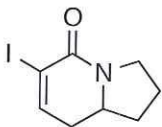
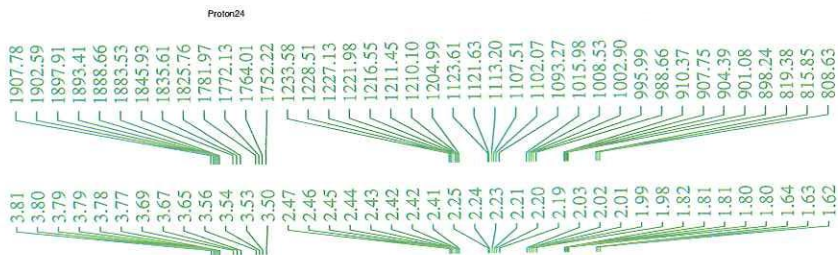
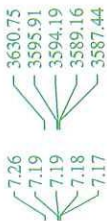
NMR Analytical Core Facility  
 Rockefeller Research Laboratories  
 430 E 71st St  
 New York, NY 10021

Current Data Parameters  
 NAME AL-iodide  
 EXPNO 1  
 PROCNO 1

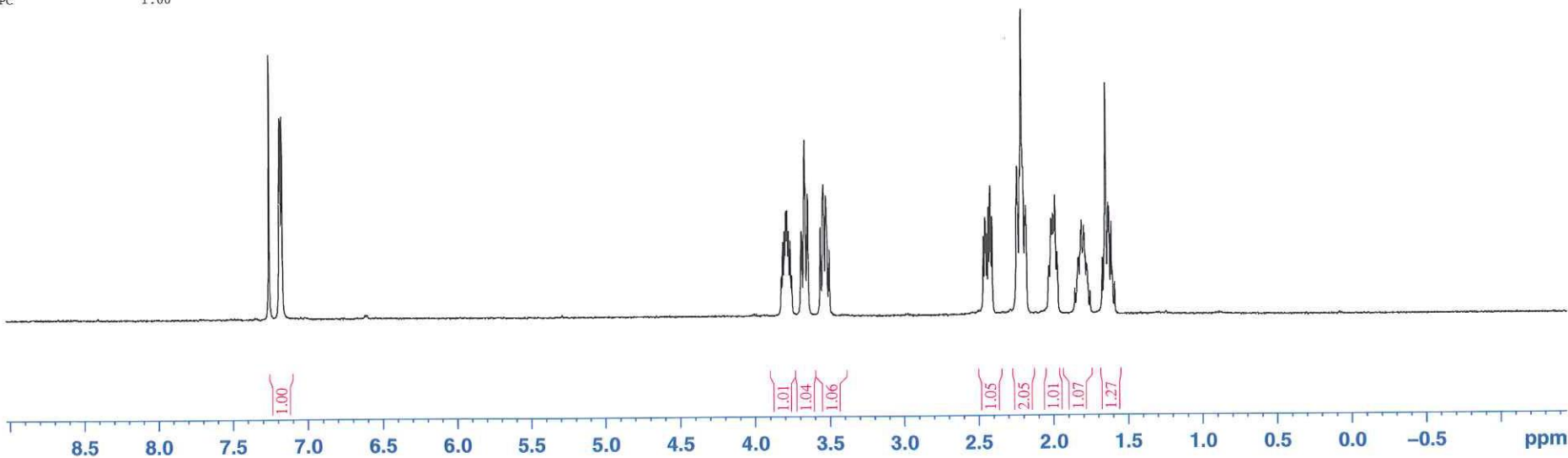
F2 - Acquisition Parameters  
 Date\_ 20140728  
 Time 13.21  
 INSTRUM spect  
 PROBHD 5 mm QNP 1H/13  
 PULPROG zg30  
 TD 32768  
 SOLVENT CDC13  
 NS 9  
 DS 0  
 SWH 10964.912 Hz  
 FIDRES 0.334623 Hz  
 AQ 1.4942708 sec  
 RG 724.1  
 DW 45.600 usec  
 DE 6.00 usec  
 TE 297.2 K  
 D1 1.00000000 sec  
 TD0 1

===== CHANNEL f1 =====  
 NUC1 1H  
 P1 14.00 usec  
 PL1 -1.00 dB  
 SFO1 500.1340010 MHz

F2 - Processing parameters  
 SI 32768  
 SF 500.1300136 MHz  
 WDW EM  
 SSB 0  
 LB 0.30 Hz  
 GB 0  
 PC 1.00

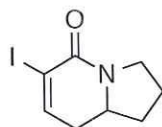


500 MHz, <sup>13</sup>CDCl<sub>3</sub>  
 S-5



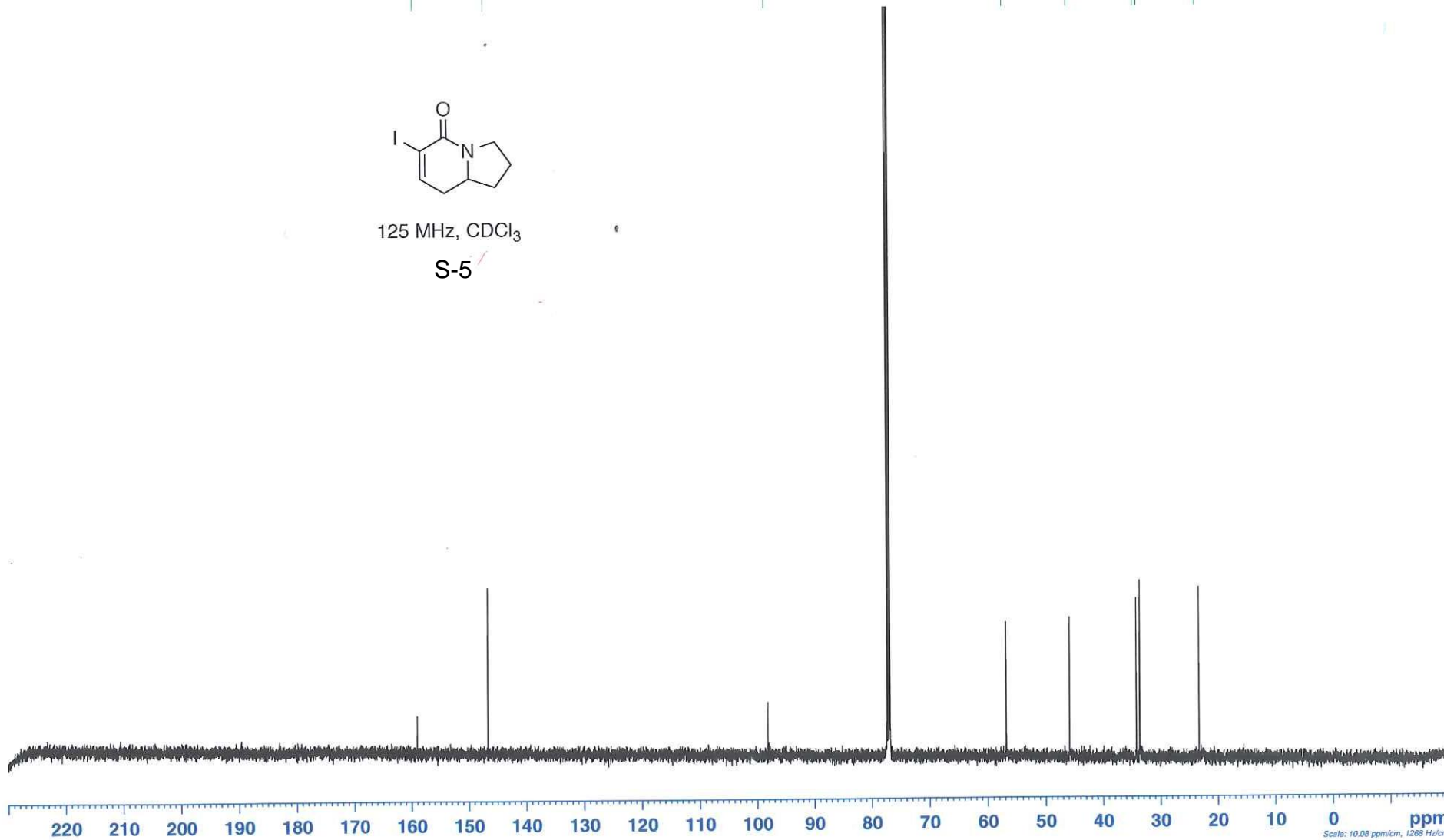
Carbon

159.12 — 20010.51  
146.77 — 18458.08  
98.16 — 12344.82  
56.90 — 7155.00  
45.83 — 5763.61  
34.19 — 4300.07  
33.59 — 4224.59  
23.30 — 2930.04



125 MHz, CDCl<sub>3</sub>

S-5







NMR Analytical Core Facility  
chefeller Research Laboratories  
430 E 67th St  
New York, NY 10021

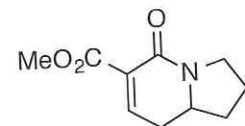
group Danishefsky  
.\*townsens al-3-084 (10 1) CDCI3 24.0C May\_25,2014\_11:15:15 Bruker AVIII 600MHz RRL1326: janggeum zg30 : 1H 7.500 ppm \*.  
\_ProtonBC CDCl3 /opt/users/townsens townsens 12

7.35  
7.35  
7.34  
7.34  
7.26

3.83  
3.74  
3.73  
3.73  
3.66  
3.66  
3.65  
3.64  
3.54  
3.53  
3.52  
3.51  
3.50  
3.49  
2.64  
2.63  
2.63  
2.62  
2.61  
2.60  
2.60  
2.59  
2.27  
2.26  
2.24  
2.24  
2.24  
2.23  
2.21  
2.21  
2.05  
2.04  
2.04  
2.03  
1.83  
1.82  
1.81  
1.81  
1.65

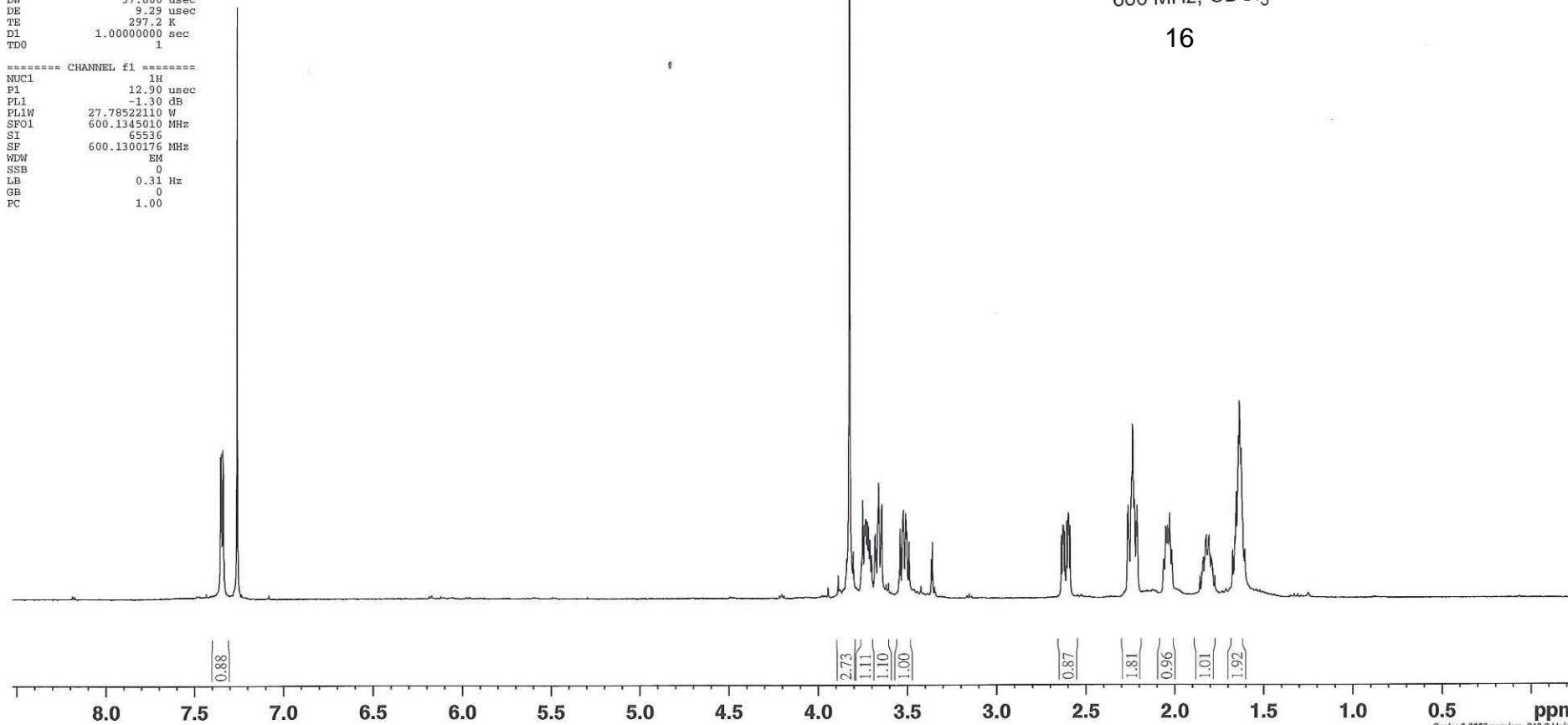
NAME al-3-084  
EXPNO 10  
PROCNO 1  
Date\_ 20140525  
Time 11.16  
INSTRUM spect  
PROBHD 5 mm PATXO 19P  
PULPROG zg30  
TD 65536  
SOLVENT CDCl3  
NS 24  
DS 0  
SWH 13227.514 Hz  
FIDRES 0.201836 Hz  
AQ 2.4773109 sec  
RG 322  
DW 37.800 usec  
DE 9.29 usec  
TE 297.2 K  
D1 1.00000000 sec  
TDO 1

\*\*\*\*\* CHANNEL f1 \*\*\*\*\*  
NUC1 1H  
P1 12.90 usec  
PL1 -1.30 dB  
PL1W 27.78522110 W  
SFO1 600.1345010 MHz  
SI 65536  
SF 600.1300176 MHz  
WDW EM  
SSB 0  
LB 0.31 Hz  
GB 0  
PC 1.00



600 MHz, CDCl<sub>3</sub>

16



Scale: 0.3553 ppm/cm, 213.2 Hz/cm

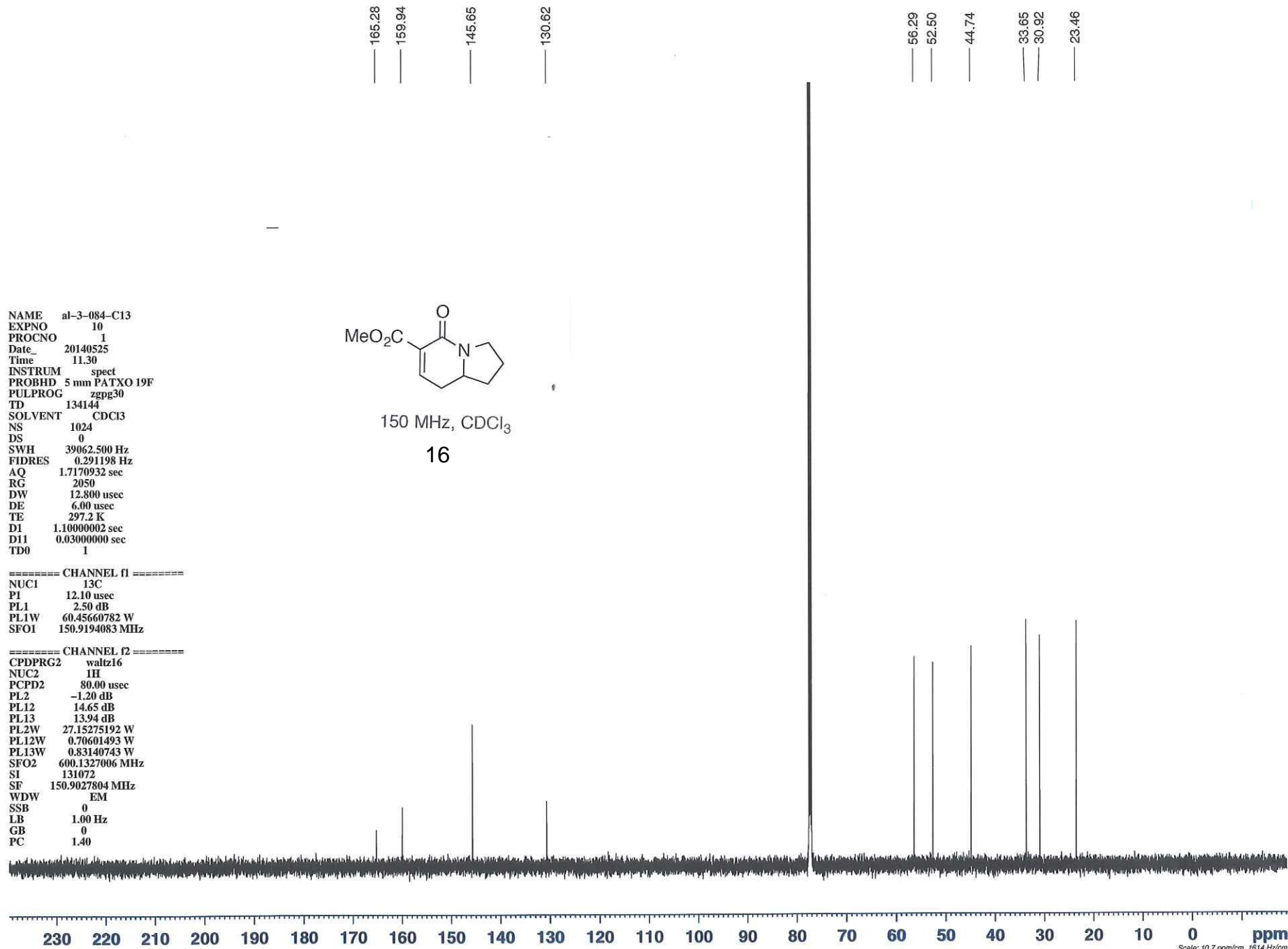
NAME al-3-084-C13  
EXPNO 10  
PROCNO 1  
Date\_ 20140525  
Time 11.30  
INSTRUM spect  
PROBHD 5 mm PATXO 19F  
PULPROG zgpg30  
TD 134144  
SOLVENT CDCl3  
NS 1024  
DS 0  
SWH 39062.500 Hz  
FIDRES 0.291198 Hz  
AQ 1.7170932 sec  
RG 2050  
DW 12.800 usec  
DE 6.00 usec  
TE 297.2 K  
D1 1.10000002 sec  
D11 0.03000000 sec  
TD0 1



16

===== CHANNEL f1 =====  
NUC1 13C  
P1 12.10 usec  
PL1 2.50 dB  
SFO1 60.45660782 W  
SFO1 150.9194083 MHz

===== CHANNEL f2 =====  
CPDPRG2 waltz16  
NUC2 1H  
PCPD2 80.00 usec  
PL2 -1.20 dB  
PL12 14.65 dB  
PL13 13.94 dB  
PL2W 27.15275192 W  
PL12W 0.70601493 W  
PL13W 0.83140743 W  
SFO2 600.1327006 MHz  
SI 131072  
SF 150.9027804 MHz  
WDW EM  
SSB 0  
LB 1.00 Hz  
GB 0  
PC 1.40





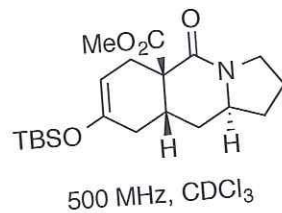
IBM Analytical Core Facility  
Rockefeller Research Laboratories  
430 E 67th St  
New York, NY 10021

Current Data Parameters  
NAME al-1-187-purified  
EXPNO 1  
PROCNO 1

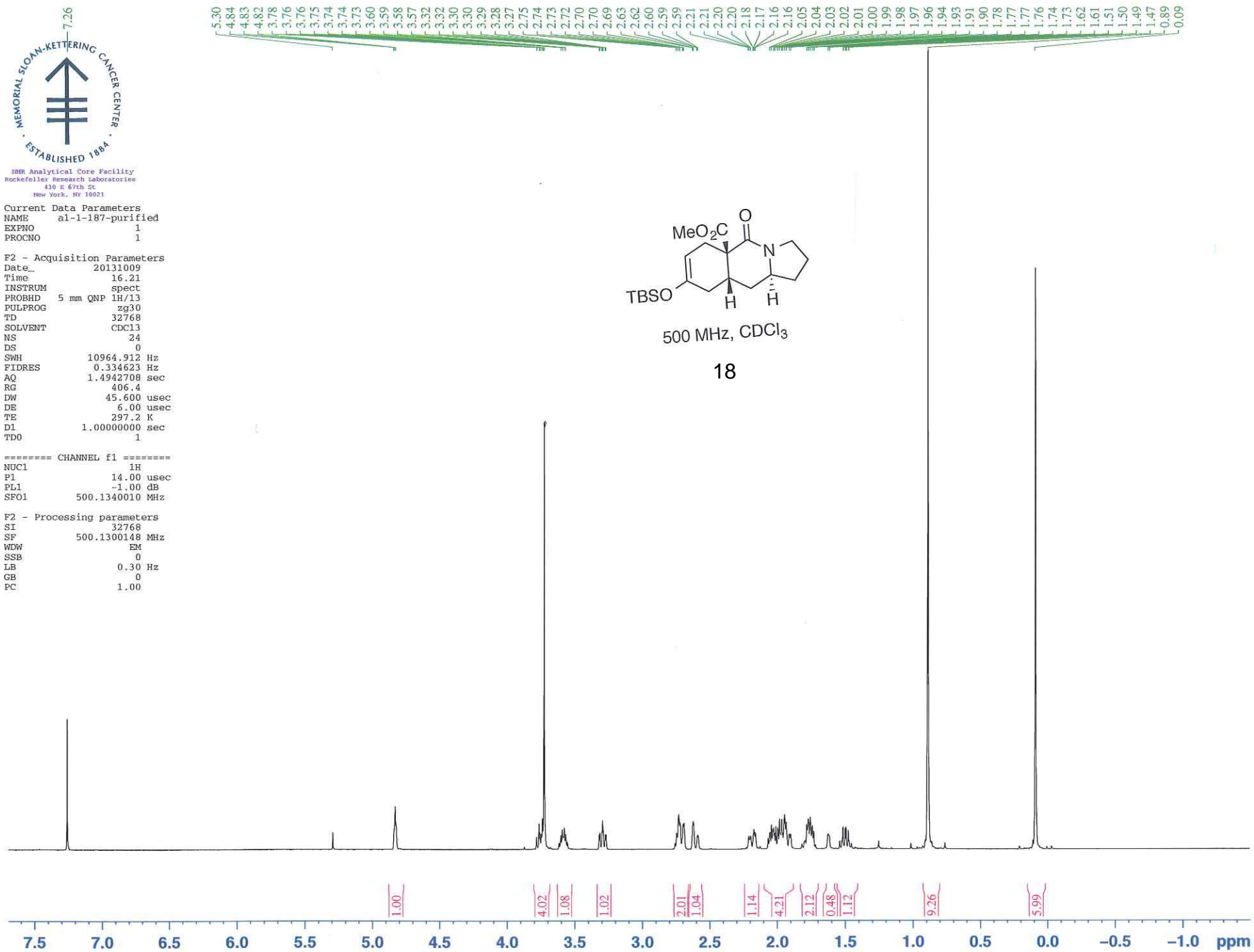
F2 - Acquisition Parameters  
Date\_ 20131009  
Time 16.21  
INSTRUM spect  
PROBHD 5 mm QNP 1H/13  
PULPROG zg30  
TD 32768  
SOLVENT CDCl3  
NS 24  
DS 0  
SWH 10964.912 Hz  
FIDRES 0.334623 Hz  
AQ 1.4942708 sec  
RG 406.4  
DW 45.600 usec  
DE 6.00 usec  
TE 297.2 K  
D1 1.00000000 sec  
TD0 1

===== CHANNEL f1 =====  
NUC1 1H  
P1 14.00 usec  
PL1 -1.00 dB  
SFO1 500.1340010 MHz

F2 - Processing parameters  
SI 32768  
SF 500.1300148 MHz  
WDW EM  
SSB 0  
LB 0.30 Hz  
GB 0  
PC 1.00



18





NMR Analytical Core Facility  
Rockefeller Research Laboratories  
430 E. 67th St.  
New York, NY 10021

173.47

168.29

148.17

Carbon  
125

55.05

53.57

52.67

44.58

33.81

32.82

31.87

29.15

26.78

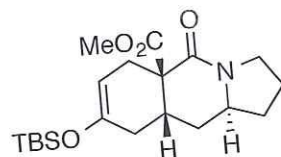
25.75

22.10

18.07

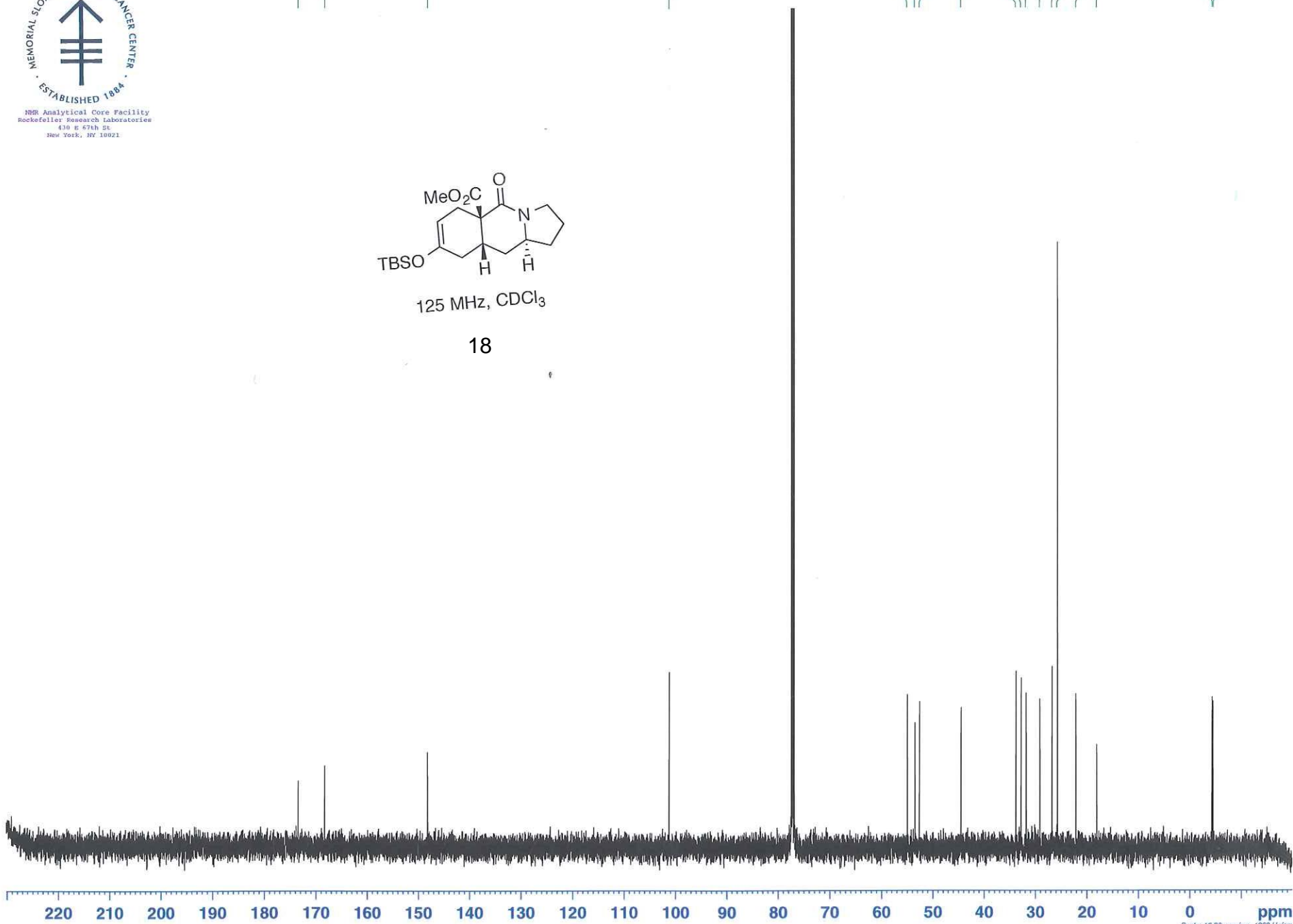
-4.33

-4.49



125 MHz, CDCl<sub>3</sub>

18



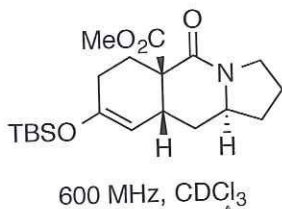
Scale: 10.08 ppm/cm, 1268 Hz/cm



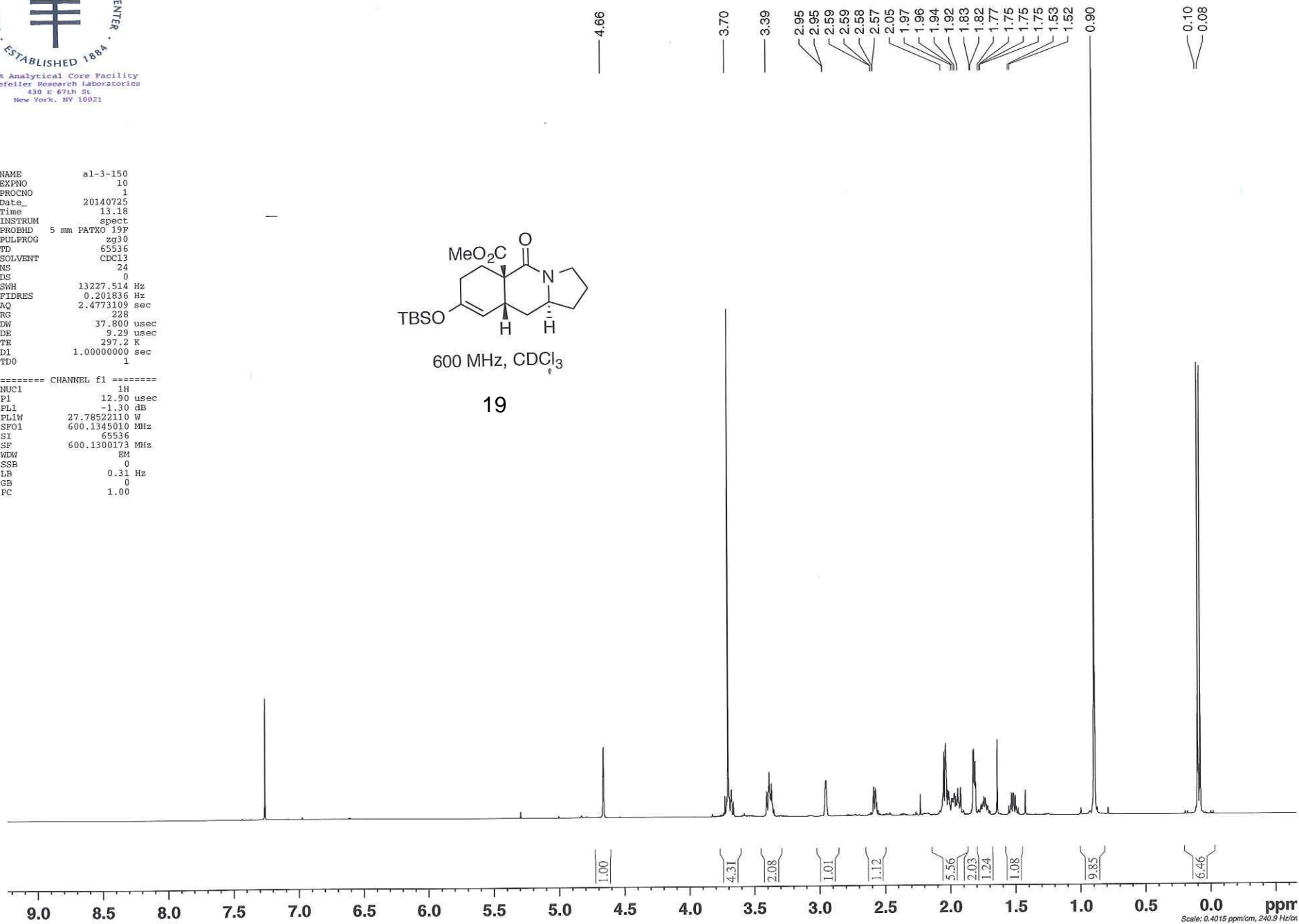
NMR Analytical Core Facility  
 Ckefeller Research Laboratories  
 430 E 67th St  
 New York, NY 10021

group Danishefsky  
 \* levinsoa al-3-150 (10 1) CDCl3 24.0C July\_25,2014\_13:16:45 Bruker AVIII 600MHz RRL1326: janggeum zg30 : 1H 7.500 ppm \*  
 \_ProtonBC CDCl3 /opt/users/levinsoa levinsoa 23

NAME al-3-150  
 EXPNO 10  
 PROCNO 1  
 Date\_ 20140725  
 Time 13.18  
 INSTRUM spect  
 PROBHD 5 mm PATXO 19F  
 PULPROG zg30  
 TD 65536  
 SOLVENT CDCl3  
 NS 24  
 DS 0  
 SWH 13227.514 Hz  
 FIDRES 0.201836 Hz  
 AQ 2.4773109 sec  
 RG 228  
 DW 37.800 usec  
 DE 9.29 usec  
 TE 297.2 K  
 D1 1.0000000 sec  
 TD0 1

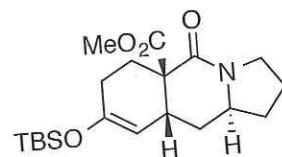


19



Scale: 0.4015 ppm/cm, 240.9 Hz/cm

NAME al-3-150  
EXPNO 11  
PROCNO 1  
Date\_ 20140725  
Time 14.08  
INSTRUM spect  
PROBHD 5 mm PATXO 19F  
PULPROG zgpg30  
TD 134144  
SOLVENT CDCl3  
NS 1024  
DS 0  
SWH 39062.500 Hz  
FIDRES 0.291198 Hz  
AQ 1.7170932 sec  
RG 2050  
DW 12.800 usec  
DE 6.00 usec  
TE 297.2 K  
D1 1.10000002 sec  
D11 0.03000000 sec  
TD0 1

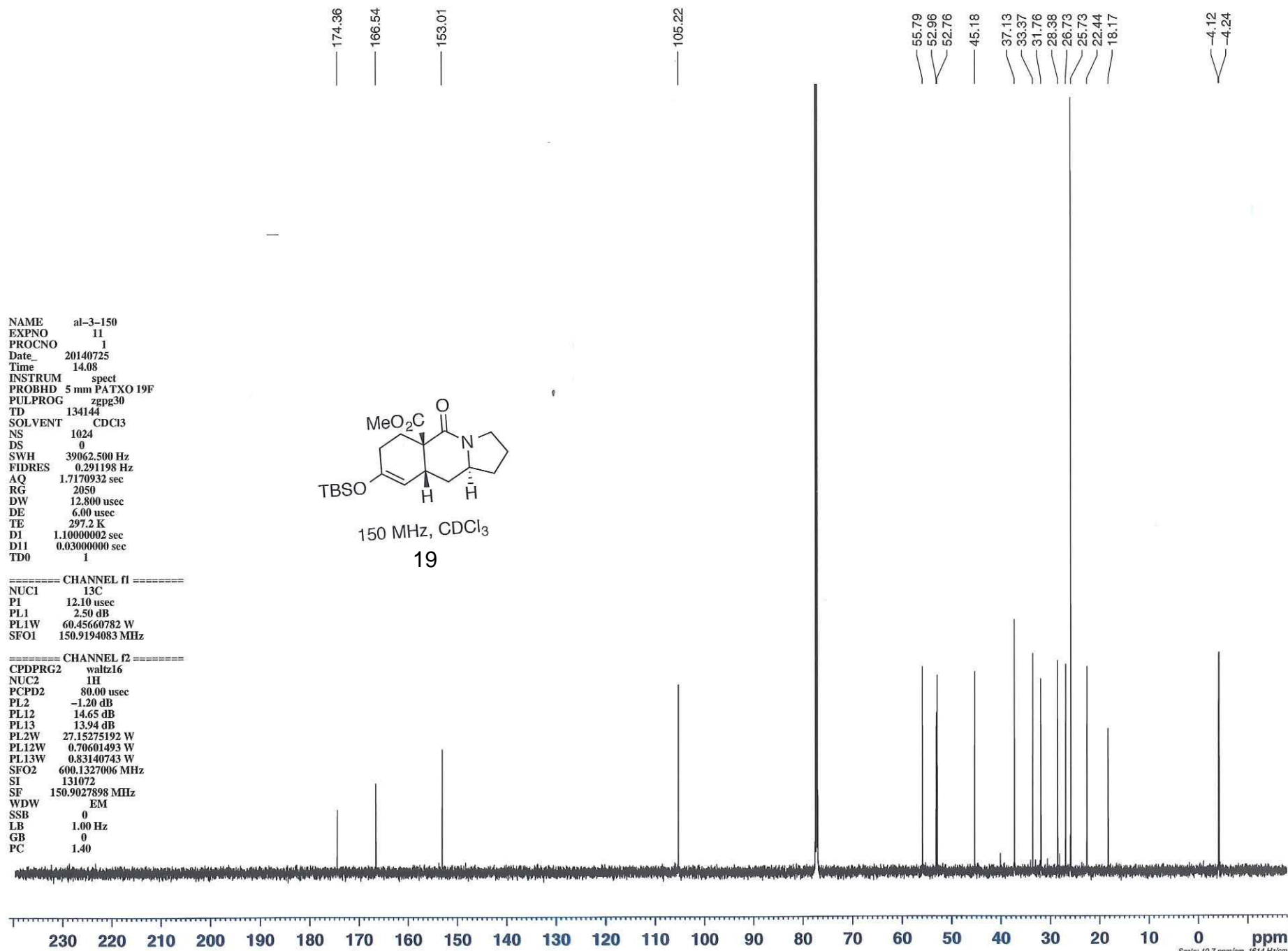


150 MHz, CDCl<sub>3</sub>

19

===== CHANNEL f1 =====  
NUC1 13C  
P1 12.10 usec  
PL1 2.50 dB  
PL1W 60.45660782 W  
SFO1 150.9194083 MHz

===== CHANNEL f2 =====  
CPDPRG2 waltz16  
NUC2 1H  
PCPD2 80.00 usec  
PL2 -1.20 dB  
PL12 14.65 dB  
PL13 13.94 dB  
PL2W 27.15275192 W  
PL12W 0.70601493 W  
PL13W 0.83140743 W  
SFO2 600.1327006 MHz  
SI 131072  
SF 150.9027898 MHz  
WDW EM  
SSB 0  
LB 1.00 Hz  
GB 0  
PC 1.40



Scale: 10.7 ppm/cm, 1614 Hz/cm





NMR Analytical Core Facility  
 Cheffler Research Laboratories  
 430 E 67th St  
 New York, NY 10021

group Danishefsky  
 \* levinsoa aspeverin-enone-2 (10 1) CDCl<sub>3</sub> 24.0C July\_24\_2014\_17:36:40 Bruker AVIII 600MHz RRL1326: janggeum zg30 : 1H 7.500 ppm \*  
 \_ProtonBC CDCl<sub>3</sub> /opt/users/levinsoa levinsoa 33

7.26  
 5.96  
 3.75  
 3.69  
 3.67  
 3.67  
 3.66  
 3.65  
 3.64  
 3.53  
 3.51  
 3.49  
 3.47  
 3.46  
 3.45  
 3.44  
 3.43  
 3.42  
 3.05  
 3.04  
 3.04  
 3.03  
 3.02  
 3.02  
 3.02  
 3.01  
 2.96  
 2.95  
 2.93  
 2.93  
 2.92  
 2.90  
 2.89  
 2.85  
 2.85  
 2.83  
 2.81  
 2.81  
 2.78  
 2.77  
 2.76  
 2.75  
 2.53  
 2.52  
 2.52  
 2.50  
 2.50  
 2.49  
 2.26  
 2.25  
 2.24  
 2.23  
 2.22  
 2.08  
 2.07  
 2.06  
 2.05  
 2.03  
 2.00  
 1.99  
 1.98  
 1.97  
 1.95  
 1.94  
 1.86

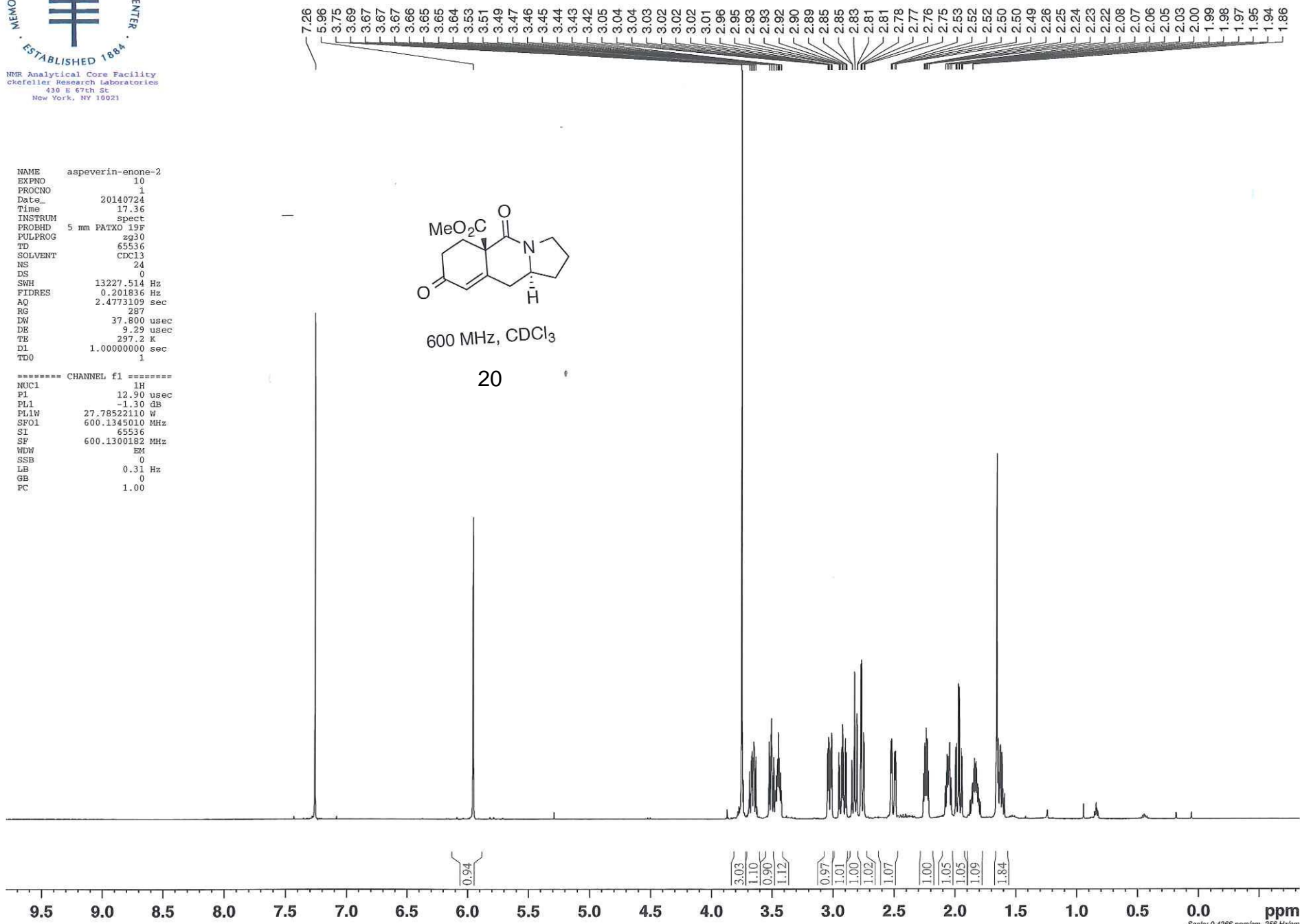
NAME aspeverin-enone-2  
 EXPNO 10  
 PROCNO 1  
 Date\_ 20140724  
 Time 17.36  
 INSTRUM spect  
 PROBHD 5 mm PATXO 19F  
 PULPROG zg30  
 TD 65536  
 SOLVENT CDCl<sub>3</sub>  
 NS 24  
 DS 0  
 SWH 13227.514 Hz  
 FIDRES 0.201836 Hz  
 AQ 2.4773109 sec  
 RG 287  
 DW 37.800 usec  
 DE 9.29 usec  
 TE 297.2 K  
 D1 1.00000000 sec  
 TDO 1



600 MHz, CDCl<sub>3</sub>

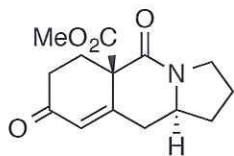
20

===== CHANNEL f1 =====  
 NUC1 1H  
 P1 12.90 usec  
 PL1 -1.30 dB  
 PL1W 27.78522110 W  
 SFO1 600.1345010 MHz  
 S1 65536  
 SF 600.1300182 MHz  
 WDW EM  
 SSB 0  
 LB 0.31 Hz  
 GB 0  
 PC 1.00



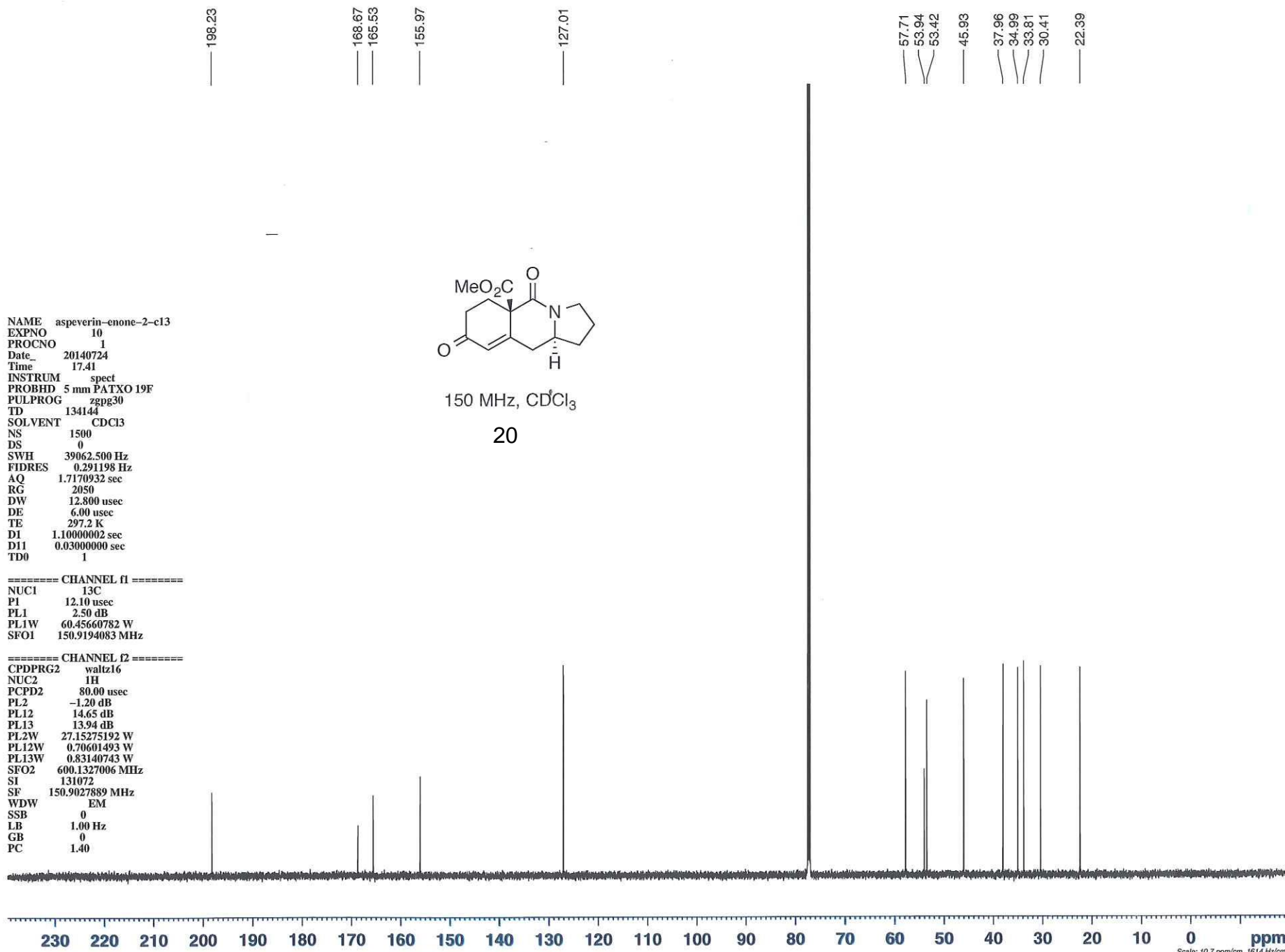
Scale: 0.4266 ppm/cm, 256 Hz/cm

NAME aspeverin-enone-2-c13  
 EXPNO 10  
 PROCNO 1  
 Date\_ 20140724  
 Time 17.41  
 INSTRUM spect  
 PROBHD 5 mm PATXO 19F  
 PULPROG zgpg30  
 TD 134144  
 SOLVENT CDCl3  
 NS 1500  
 DS 0  
 SWH 39062.500 Hz  
 FIDRES 0.291198 Hz  
 AQ 1.7170932 sec  
 RG 2050  
 DW 12.800 usec  
 DE 6.00 usec  
 TE 297.2 K  
 D1 1.10000002 sec  
 D11 0.03000000 sec  
 TD0 1



150 MHz, CDCl<sub>3</sub>

20



===== CHANNEL f1 =====  
 NUC1 13C  
 P1 12.10 usec  
 PL1 2.50 dB  
 PL1W 60.45660782 W  
 SFO1 150.9194083 MHz

===== CHANNEL f2 =====  
 CPDPRG2 waltz16  
 NUC2 1H  
 PCPD2 80.00 usec  
 PL2 -1.20 dB  
 PL12 14.65 dB  
 PL13 13.94 dB  
 PL2W 27.15275192 W  
 PL12W 0.70601493 W  
 PL13W 0.83140743 W  
 SFO2 600.1327006 MHz  
 SI 131072  
 SF 150.9027889 MHz  
 WDW EM  
 SSB 0  
 LB 1.00 Hz  
 GB 0  
 PC 1.40





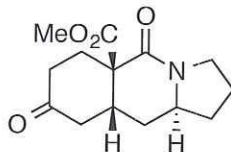
IBM Analytical Core Facility  
Rockefeller Research Laboratories  
430 E 67th St  
New York, NY 10021

Current Data Parameters  
NAME al-3-149  
EXPNO 1  
PROCNO 1

F2 - Acquisition Parameters  
Date\_ 20140724  
Time 16.29  
INSTRUM spect  
PROBHD 5 mm QNP 1H/13  
PULPROG zg30  
TD 32768  
SOLVENT CDCl3  
NS 17  
DS 0  
SWH 10964.912 Hz  
FIDRES 0.334623 Hz  
AQ 1.4942708 sec  
RG 456.1  
DW 45.600 usec  
DE 6.00 usec  
TE 297.2 K  
D1 1.00000000 sec  
TDO 1

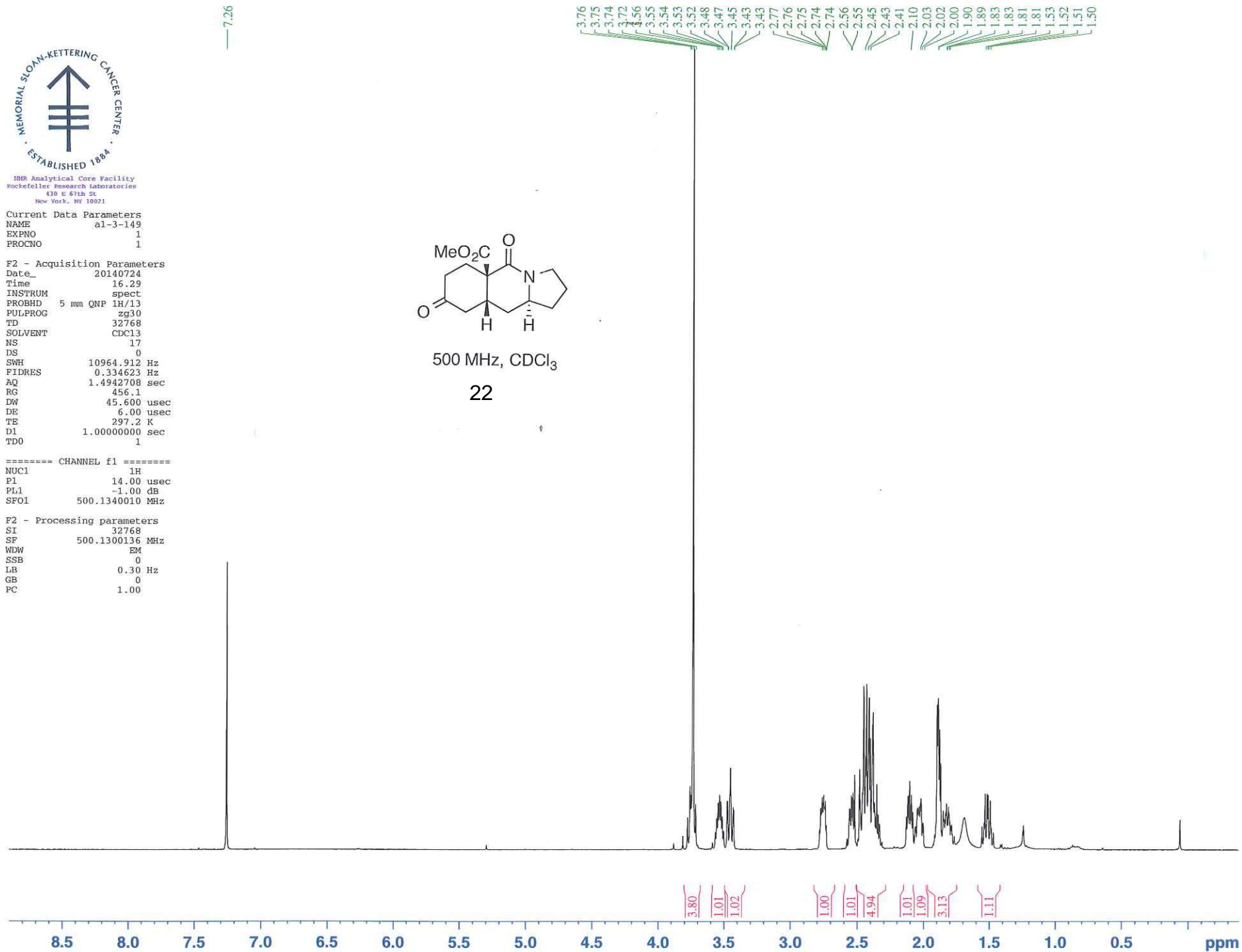
===== CHANNEL f1 =====  
NUC1 1H  
P1 14.00 usec  
PL1 -1.00 dB  
SFO1 500.1340010 MHz

F2 - Processing parameters  
SI 32768  
SF 500.1300136 MHz  
WDW EM  
SSB 0  
LB 0.30 Hz  
GB 0  
PC 1.00



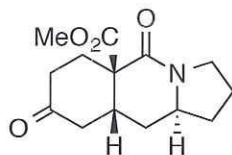
500 MHz, CDCl<sub>3</sub>

22



AL-3-149

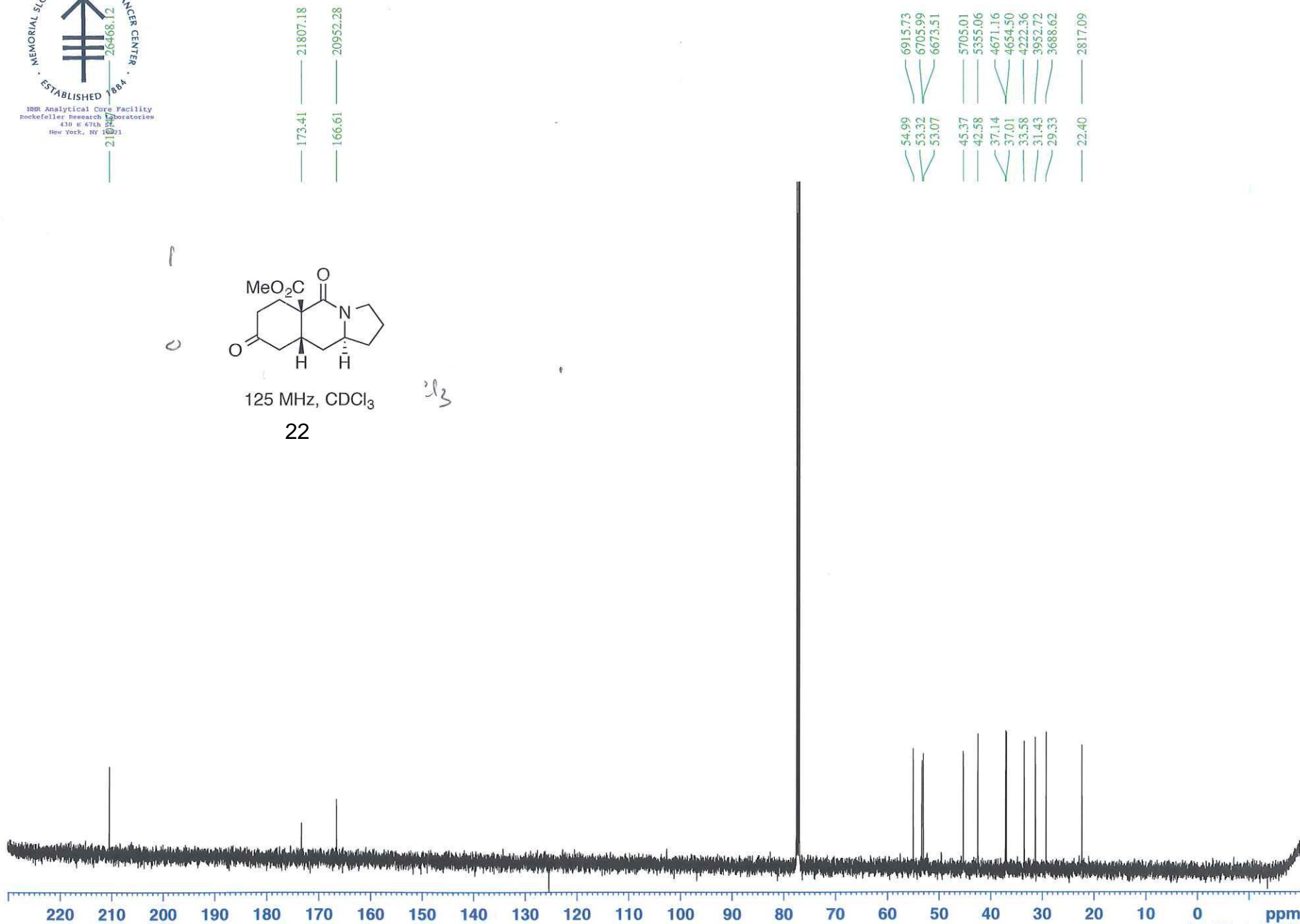
Carbon



125 MHz, CDCl<sub>3</sub>

22

23



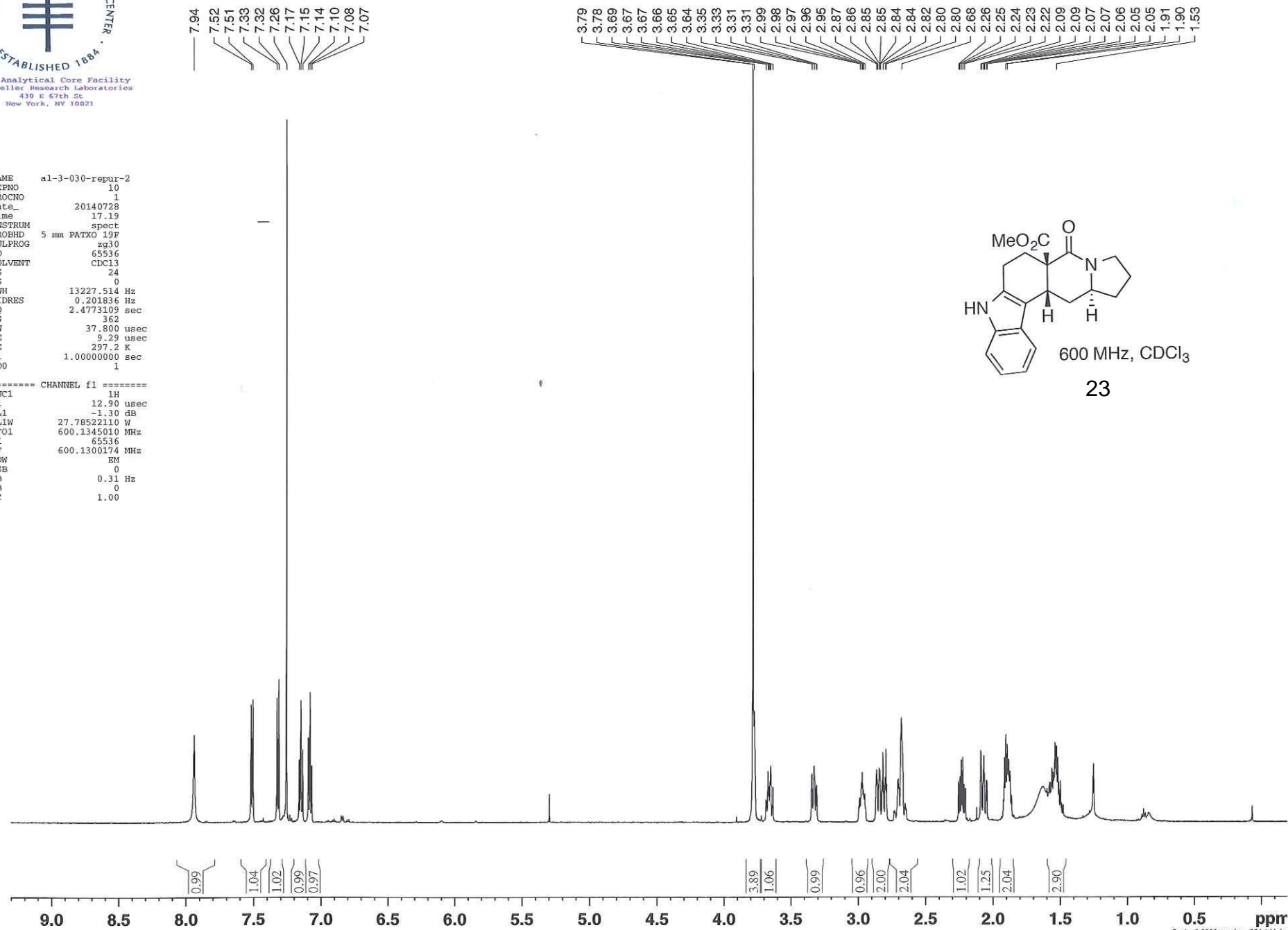


MEMORIAL SLOAN-KETTERING CANCER CENTER  
ESTABLISHED 1884  
NMR Analytical Core Facility  
Chefeller Research Laboratories  
430 E 67th St  
New York, NY 10021

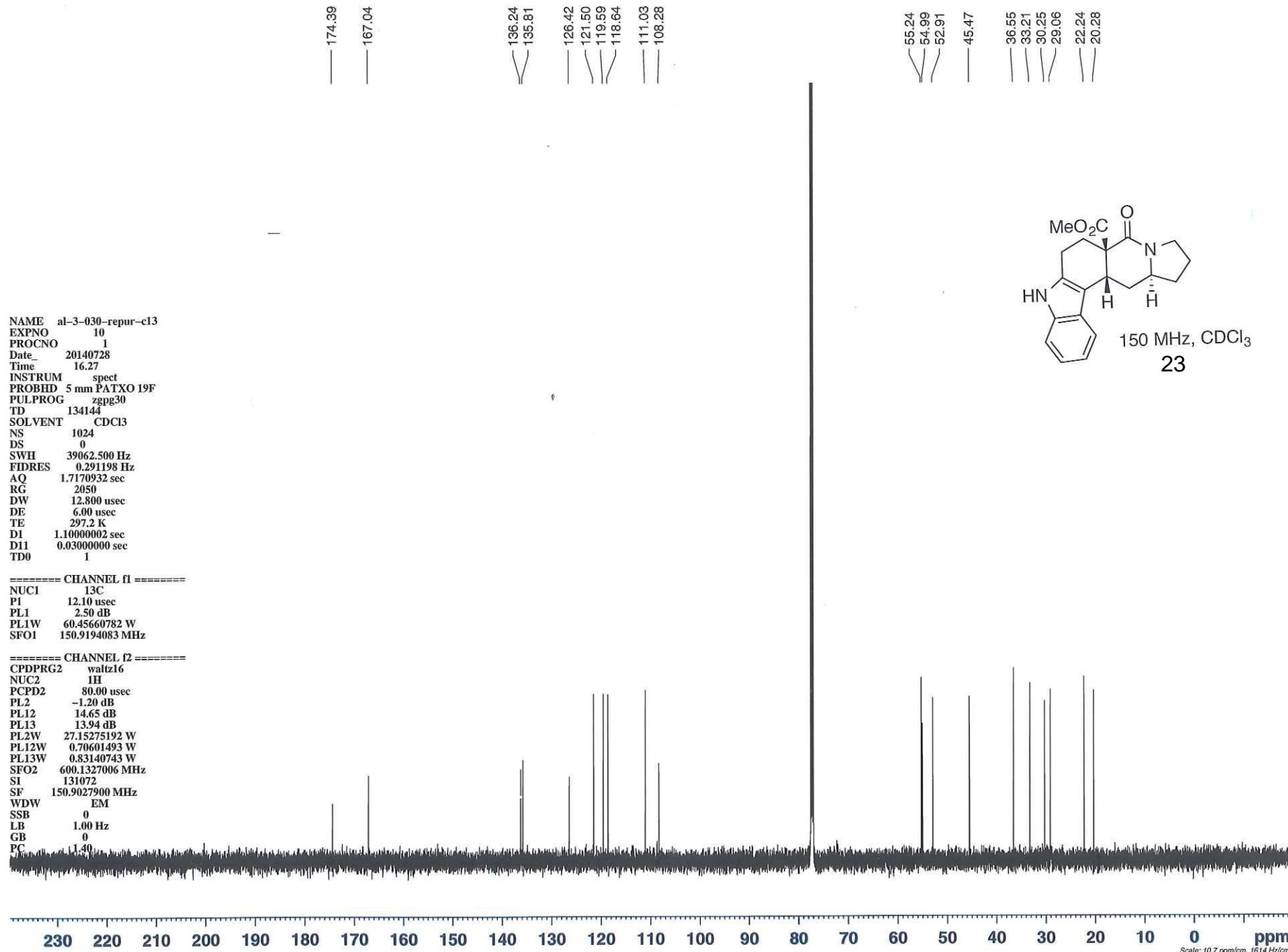
group Danishefsky  
\* levinsoa al-3-030-repur-2 (10 1) CDCl3 24.0C July\_28\_2014\_17:19:20 Bruker AVIII 600MHz RRL1326: janggeum zg30 : 1H 7.500 ppm \*  
\_ProtonBC CDCl3 /opt/users/levinsoa levinsoa 20

NAME al-3-030-repur-2  
EXPNO 10  
PROCNO 1  
Date\_ 20140728  
Time 17.19  
INSTRUM spect  
PROBHD 5 mm PATKO 19P  
PULPROG zg30  
TD 65536  
SOLVENT CDCl3  
NS 24  
DS 0  
SWH 13227.514 Hz  
FIDRES 0.201836 Hz  
AQ 2.4773109 sec  
RG 362  
DW 37.800 usec  
DE 9.29 usec  
TE 297.2 K  
D1 1.00000000 sec  
TDO 1

===== CHANNEL f1 =====  
NUC1 1H  
P1 12.90 usec  
PL1 -1.30 dB  
PL1W 27.78522110 W  
SFO1 600.1345010 MHz  
SI 65536  
SF 600.1300174 MHz  
WDW EM  
SSB 0  
LB 0.31 Hz  
GB 0  
PC 1.00



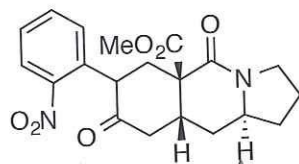
Scale: 0.3902 ppm/cm, 234.1 Hz/cm



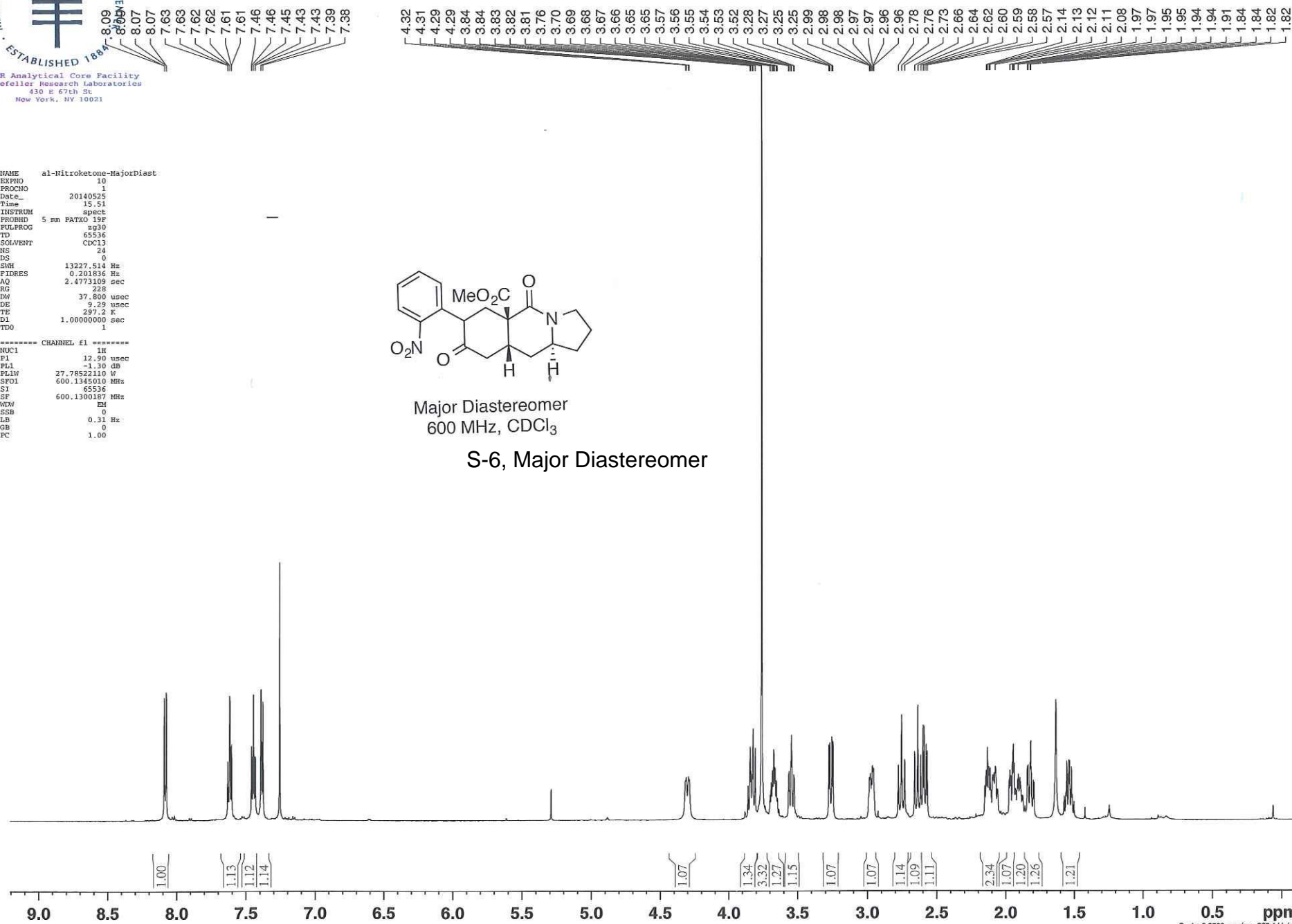
```

NAME      al-Nitroketone-MajorDiast
EXPNO     10
PROCNO    1
Date_     20140525
Time      15.51
INSTRUM   spect
PROBHD    5 mm FATQO 19F
PULPROG   zg30
TD         65536
SOLVENT   CDCl3
NS         24
DS         0
SVH       13227.514 Hz
FIDRES    0.201836 Hz
AQ         2.4773109 sec
RG         228
DW         37.800 usec
DE         9.29 usec
TE         297.2 K
D1         1.00000000 sec
TDO        1

===== CHANNEL f1 =====
NUC1      1H
P1        12.90 usec
PL1       -1.30 dB
PL1W      27.78522110 W
SFO1      600.1345010 MHz
SI         65536
SF         600.1300187 MHz
WDW        EM
SSB        0
LB         0.31 Hz
GB         0
PC         1.00
    
```



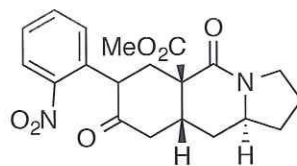
Major Diastereomer  
 600 MHz, CDCl<sub>3</sub>  
 S-6, Major Diastereomer



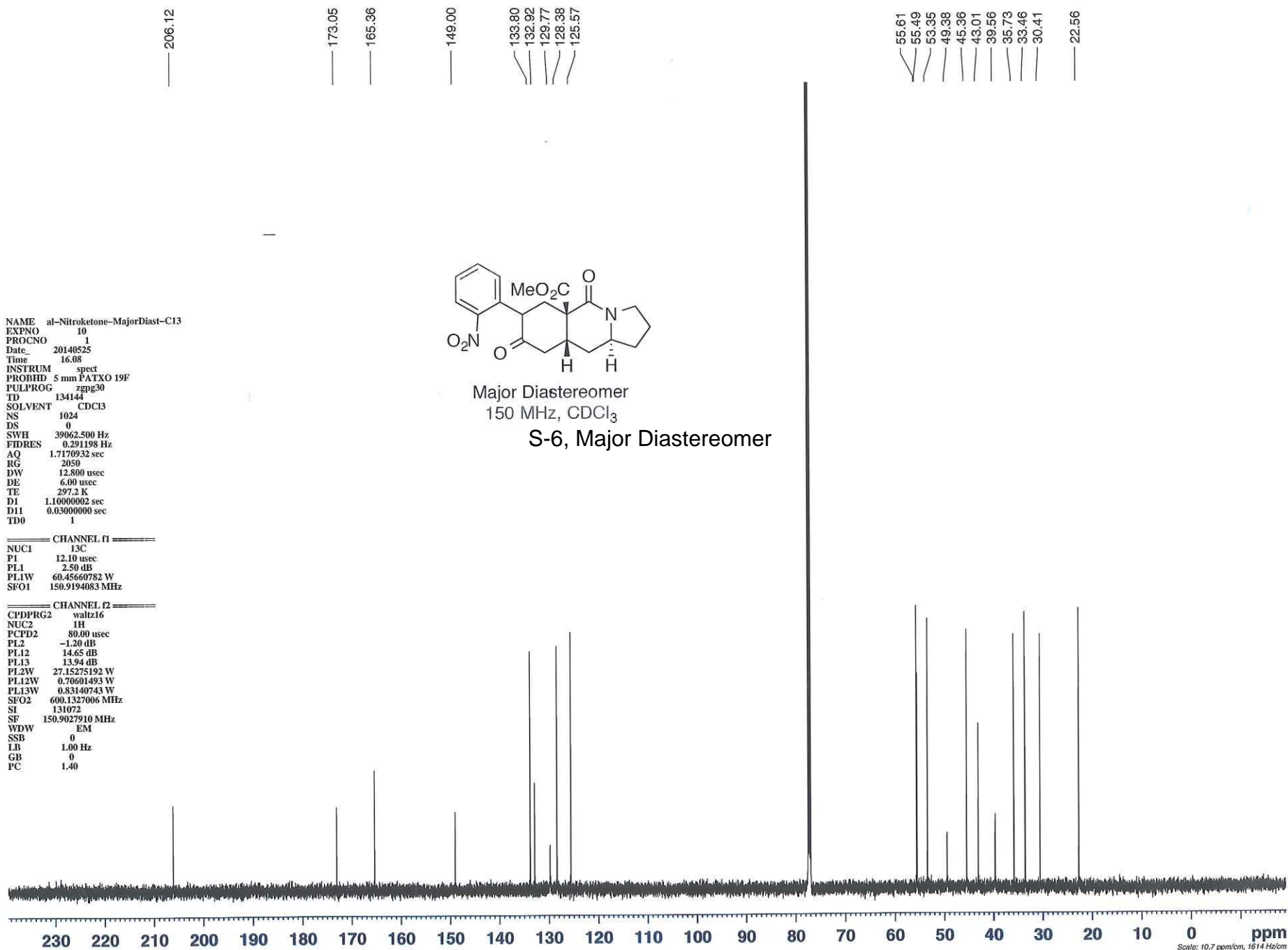
NAME al-Nitroketone-MajorDiast-C13  
 EXPNO 10  
 PROCNO 1  
 Date\_ 20140525  
 Time 16.08  
 INSTRUM spect  
 PROBHD 5 mm PATXO 19F  
 PULPROG zgpg30  
 TD 134144  
 SOLVENT CDC13  
 NS 1024  
 DS 0  
 SWH 39062.500 Hz  
 FIDRES 0.291198 Hz  
 AQ 1.7170932 sec  
 RG 2050  
 DW 12.800 usec  
 DE 6.00 usec  
 TE 297.2 K  
 D1 1.10000002 sec  
 D11 0.03000000 sec  
 TD0 1

==== CHANNEL f1 =====  
 NUC1 13C  
 P1 12.10 usec  
 PL1 2.50 dB  
 PL1W 60.45660782 W  
 SFO1 150.9194083 MHz

==== CHANNEL f2 =====  
 CPDPRG2 waltz16  
 NUC2 1H  
 PCPD2 80.00 usec  
 PL2 -1.20 dB  
 PL12 14.65 dB  
 PL13 13.94 dB  
 PL2W 27.15275192 W  
 PL12W 0.70601493 W  
 PL13W 0.83140743 W  
 SFO2 600.1327006 MHz  
 SI 131072  
 SF 150.9027910 MHz  
 WDW EM  
 SSB 0  
 LB 1.00 Hz  
 GB 0  
 PC 1.40



Major Diastereomer  
 150 MHz, CDCl<sub>3</sub>  
 S-6, Major Diastereomer



Scale: 10.7 ppm/cm, 1614 Hz/cm



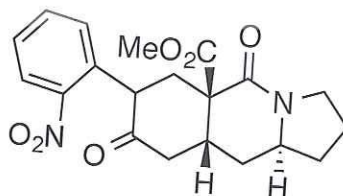


MEMORIAL SLOAN-KETTERING CANCER CENTER  
ESTABLISHED 1884  
NMR Analytical Core Facility  
Chefeller Research Laboratories  
430 E 67th St  
New York, NY 10021

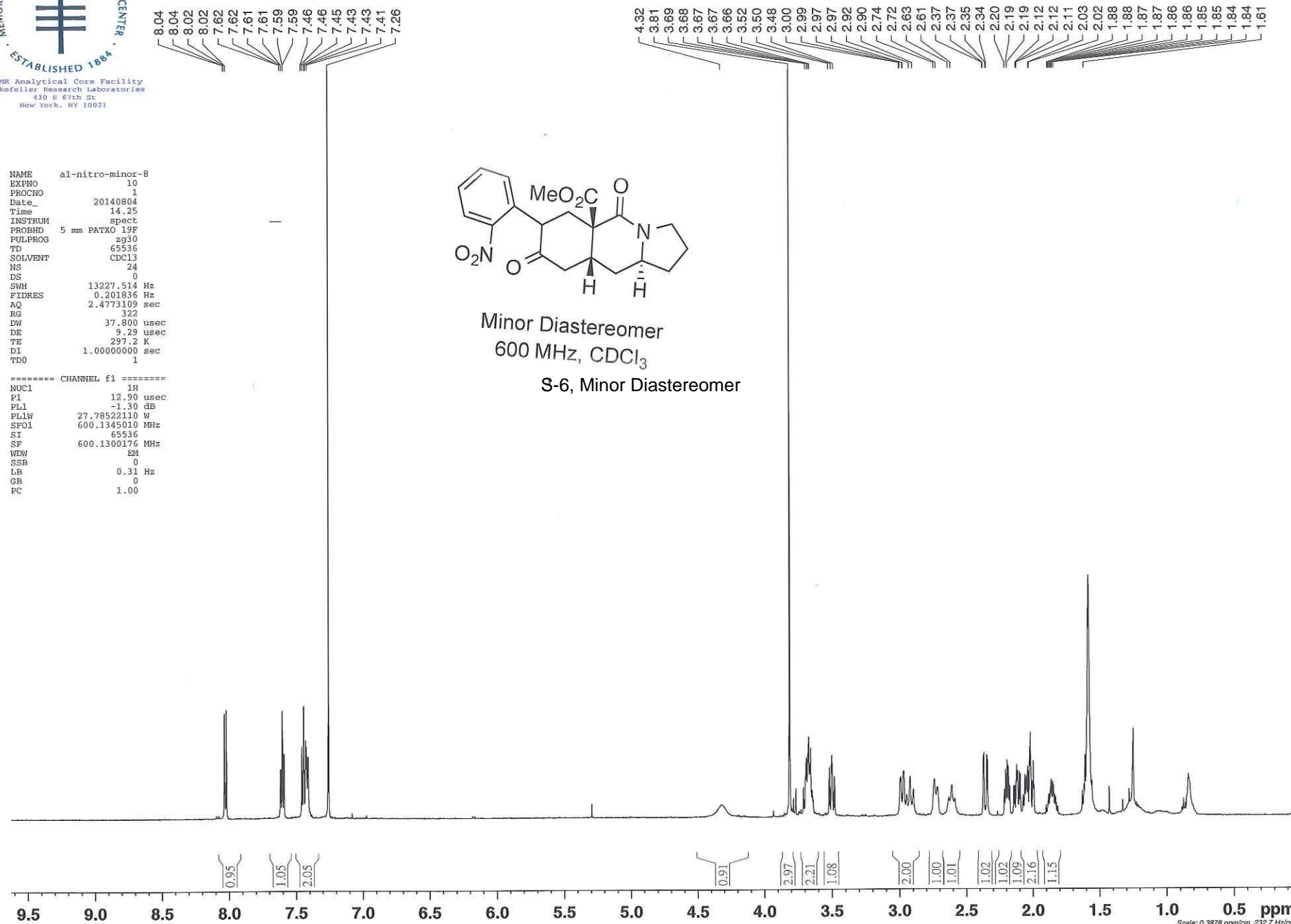
\* levinsoa al-nitro-minor-8 (10 1) CDCI3 24.0C August\_04\_2014\_14:24:03 Bruker AVIII 600MHz RRL1326: janggeum zg30 : 1H 7.500 ppm \*  
\_ProtonBC CDCI3 /opt/users/levinsoa levinsoa 42

NAME al-nitro-minor-8  
EXPNO 10  
PROCNO 1  
Date\_ 20140804  
Time 14.25  
INSTRUM spect  
PROBHD 5 mm PATKO 19F  
PULPROG zg30  
TD 65536  
SOLVENT CDCI3  
NS 24  
DS 0  
SWH 13227.514 Hz  
FIDRES 0.201836 Hz  
AQ 2.4773109 sec  
RG 322  
DW 37.800 usec  
DE 9.29 usec  
TE 297.2 K  
D1 1.00000000 sec  
TD0 1

===== CHANNEL f1 =====  
NUC1 1H  
P1 12.90 usec  
PL1 -1.30 dB  
PL1W 27.78522110 W  
SFO1 600.1345010 MHz  
SI 65536  
SF 600.1300176 MHz  
WDW EM  
SSB 0  
LB 0.31 Hz  
GB 0  
PC 1.00



Minor Diastereomer  
600 MHz, CDCl<sub>3</sub>  
S-6, Minor Diastereomer

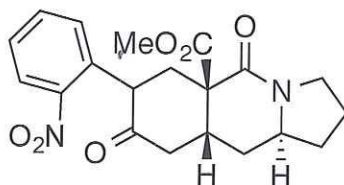




NAME: al-nitroketone-minor  
 EXPNO: 12  
 PROCNO: 1  
 Date\_: 20140804  
 Time: 16.12  
 INSTRUM: spect  
 PROBHID: 5 mm CPDCH 13C  
 PULPROG: zgpg30  
 TD: 134144  
 SOLVENT: CDCl3  
 NS: 1600  
 DS: 2  
 SWH: 52631.578 Hz  
 FIDRES: 0.392351 Hz  
 AQ: 1.274180 sec  
 RG: 287  
 DW: 9.500 usec  
 DE: 24.96 usec  
 TE: 297.2 K  
 D1: 2.00000000 sec  
 D11: 0.03000000 sec  
 TD0:

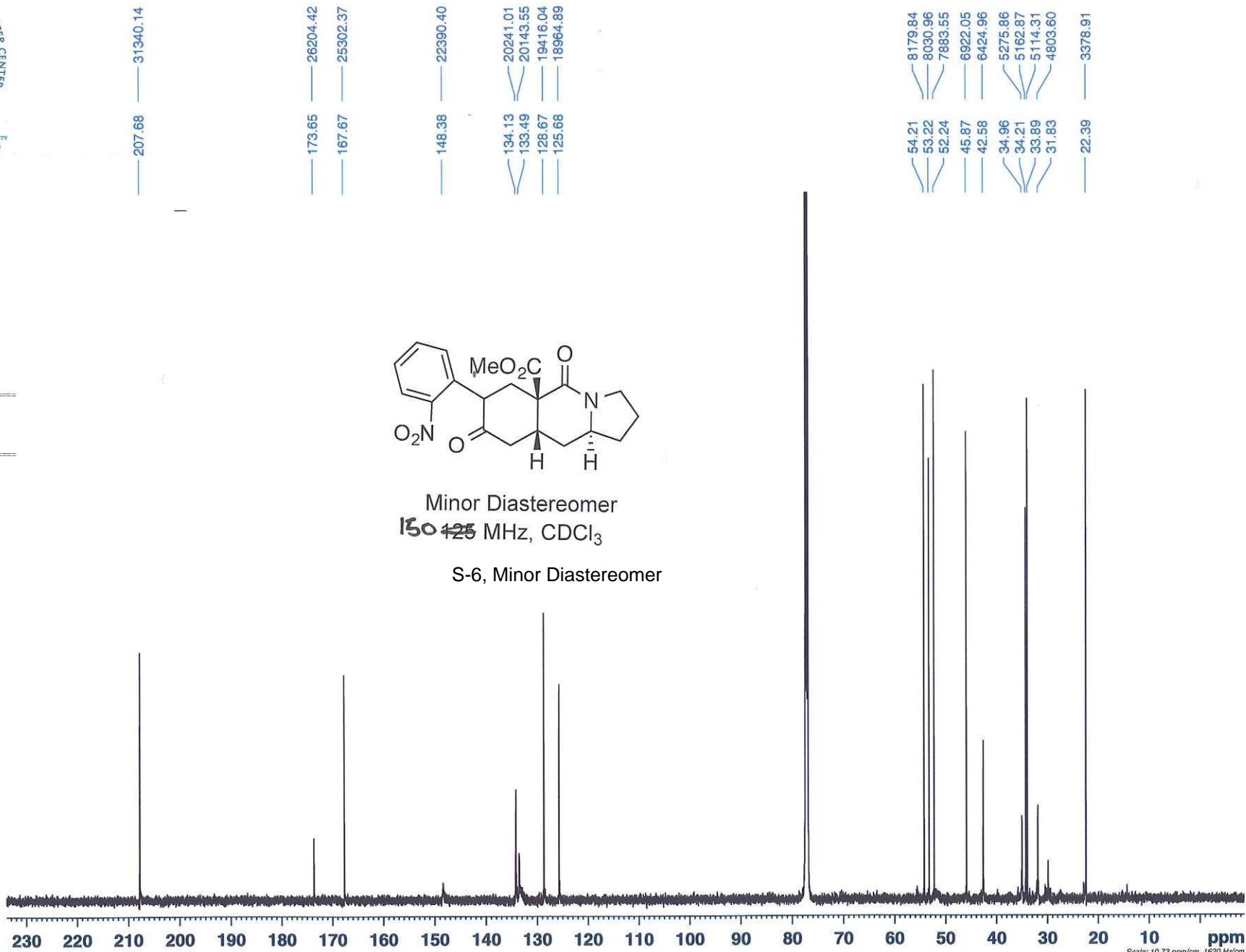
===== CHANNEL f1 =====  
 NUC1: 13C  
 P1: 9.12 usec  
 PL1: 2.60 dB  
 PL1W: 36.58018494 W  
 SFO1: 150.9224264 MHz

===== CHANNEL f2 =====  
 CPDPRG2: waltz16  
 NUC2: 1H  
 PCPD2: 70.00 usec  
 PL2: -0.70 dB  
 PL12: 14.99 dB  
 PL13: 17.99 dB  
 PL2W: 19.18285942 W  
 PL12W: 0.51750362 W  
 PL13W: 0.25936621 W  
 SFO2: 600.1324005 MHz  
 SI: 65536  
 SF: 150.9027907 MHz  
 WDW: EM  
 SSB: 0  
 LB: 1.00 Hz  
 GB: 0  
 PC: 1.40



Minor Diastereomer  
~~150.425~~ MHz, CDCl<sub>3</sub>

S-6, Minor Diastereomer







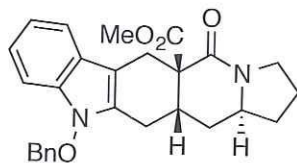
3MR Analytical Core Facility  
Rockefeller Research Laboratories  
430 E 67th St  
New York, NY 10021

Current Data Parameters  
NAME AL-2-159-clean  
EXPNO 1  
PROCNO 1

F2 - Acquisition Parameters  
Date\_ 20140206  
Time 14.17  
INSTRUM spect  
PROBHD 5 mm QNP 1H/13  
PULPROG zg30  
TD 32768  
SOLVENT CDCl3  
NS 12  
DS 0  
SWH 10964.912 Hz  
FIDRES 0.334623 Hz  
AQ 1.4942708 sec  
RG 456.1  
DW 45.600 usec  
DE 6.00 usec  
TE 297.2 K  
D1 1.00000000 sec  
TD0 1

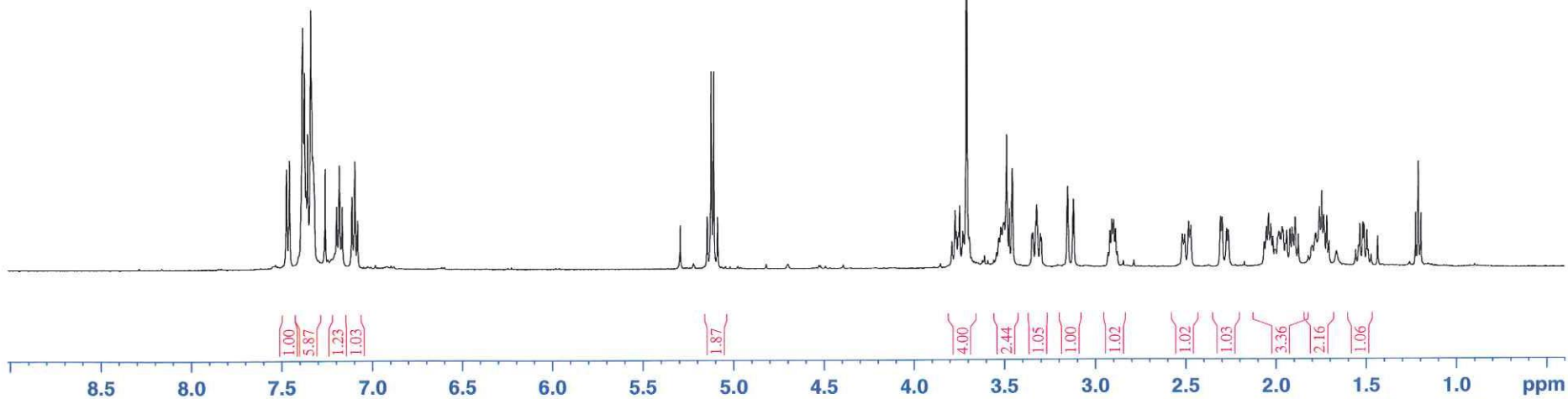
----- CHANNEL f1 -----  
NUC1 1H  
P1 14.00 usec  
PL1 -1.00 dB  
SFO1 500.1340010 MHz

F2 - Processing parameters  
SI 32768  
SF 500.1300137 MHz  
WDW EM  
SSB 0  
LB 0.30 Hz  
GB 0  
PC 1.00



500 MHz, CDCl<sub>3</sub>

25





MSK Analytical Core Facility  
Rockefeller Research Laboratories  
430 R 67th St  
New York, NY 10021

### Carbon

172.85  
168.46

134.96  
133.78  
130.75  
130.16  
129.24  
128.81  
123.37  
121.87  
119.90  
118.48

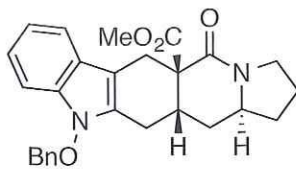
108.32  
103.17

79.50

55.00  
54.75  
52.79

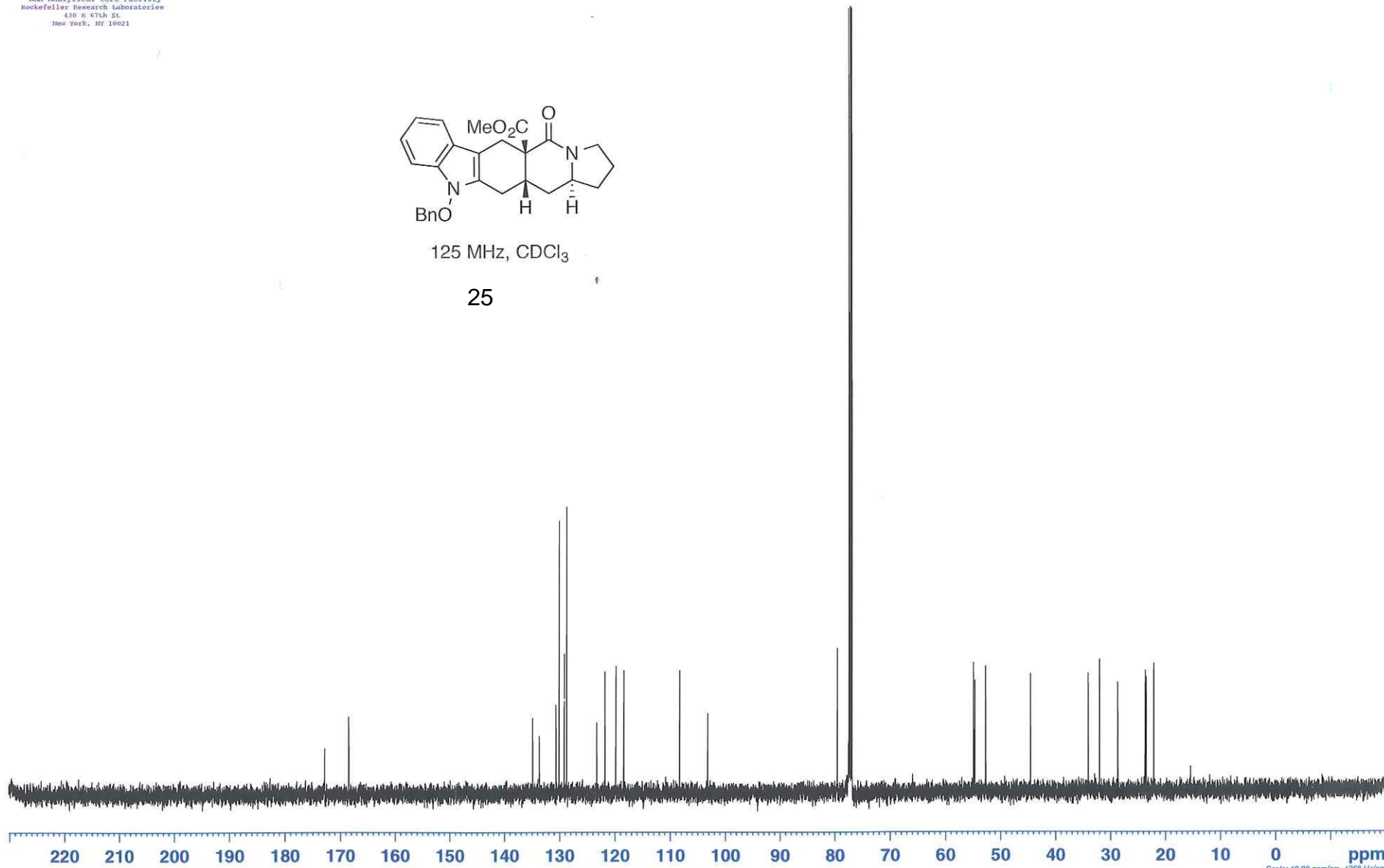
44.64

34.10  
32.01  
28.69  
23.65  
23.47  
22.12



125 MHz, CDCl<sub>3</sub>

25



Scale: 10.08 ppm/cm, 1268 Hz/cm



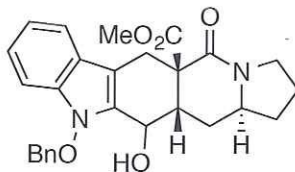
NMR Analytical Core Facility  
 Rockefeller Research Laboratories  
 430 E 67th St  
 New York, NY 10021

Current Data Parameters  
 NAME AL-3-103-2  
 EXPNO 1  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20140611  
 Time 21.54  
 INSTRUM spect  
 PROBHD 5 mm QNP 1H/13  
 PULPROG zg30  
 TD 32768  
 SOLVENT CDCl3  
 NS 22  
 DS 0  
 SWH 10964.912 Hz  
 FIDRES 0.334623 Hz  
 AQ 1.4942708 sec  
 RG 574.7  
 DW 45.600 usec  
 DE 6.00 usec  
 TE 297.2 K  
 D1 1.0000000 sec  
 TDO 1

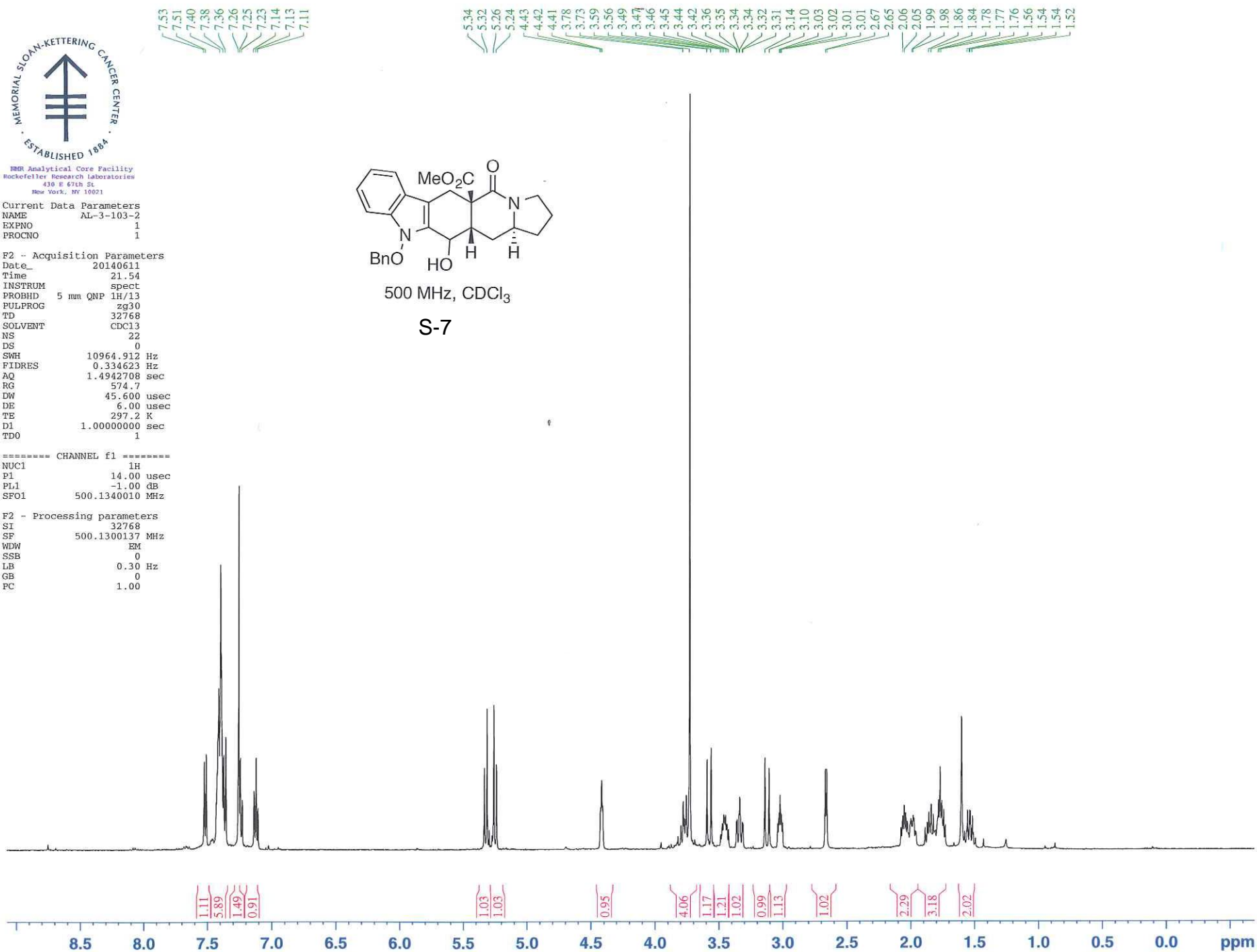
==== CHANNEL f1 =====  
 NUC1 1H  
 P1 14.00 usec  
 PL1 -1.00 dB  
 SFO1 500.1340010 MHz

F2 - Processing parameters  
 SI 32768  
 SF 500.1300137 MHz  
 WDW EM  
 SSB 0  
 LB 0.30 Hz  
 GB 0  
 PC 1.00



500 MHz, CDCl<sub>3</sub>

S-7





NMR Analytical Core Facility  
Rockefeller Research Laboratories  
130 Y 67th St  
New York, NY 10021

### Carbon

173.74  
168.06

134.96  
134.65  
131.69  
130.22  
129.39  
128.96  
123.37  
122.57  
120.34  
119.63

108.89  
105.66

80.05

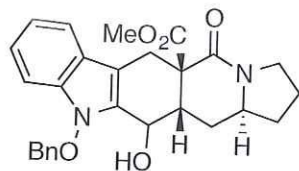
64.11

55.24  
54.19  
53.00

44.82  
41.02

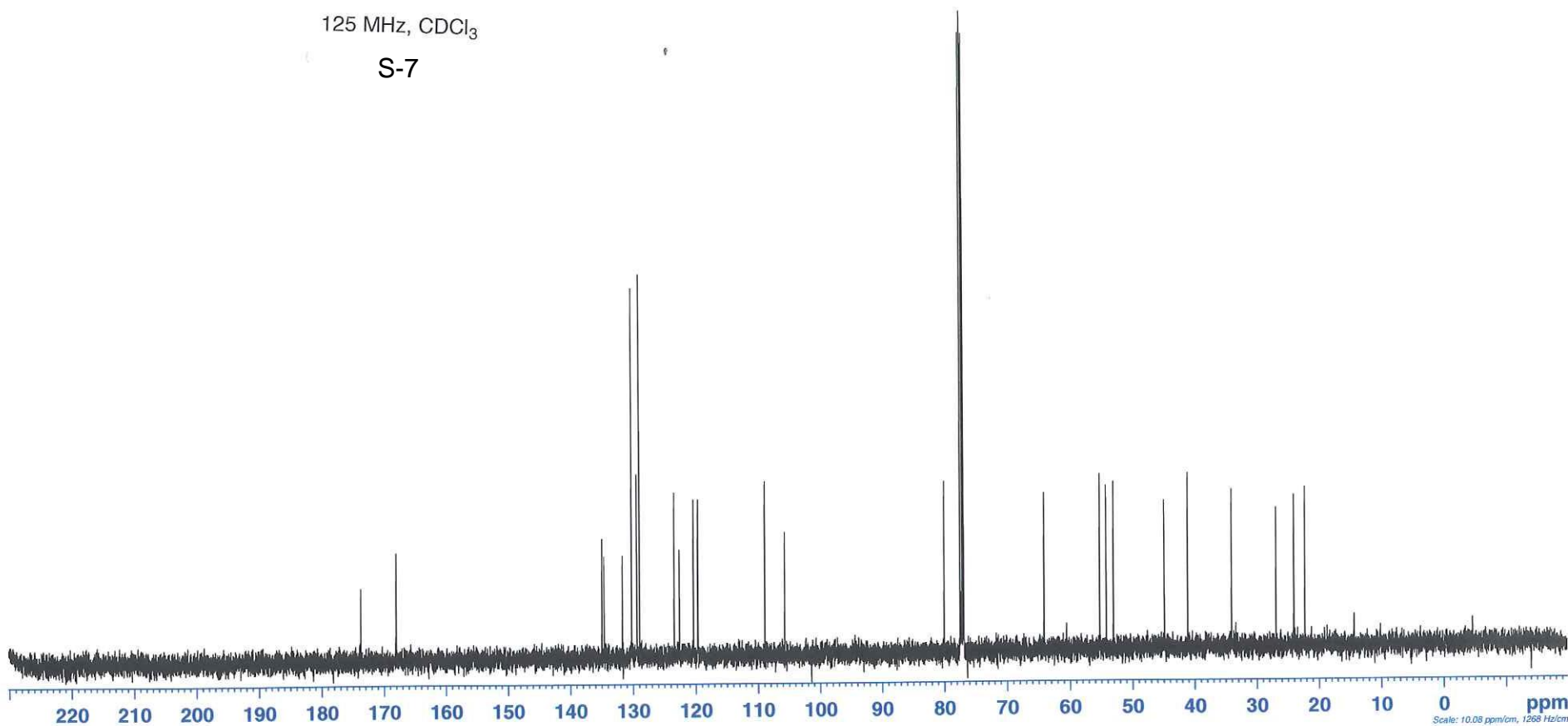
33.96

26.83  
23.99  
22.21



125 MHz, CDCl<sub>3</sub>

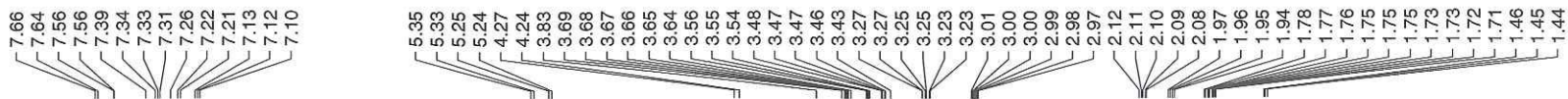
S-7



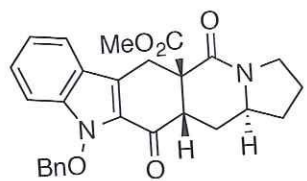


MPH Analytical Core Facility  
 Rockefeller Research Laboratories  
 430 E. 67th St.  
 New York, NY 10021

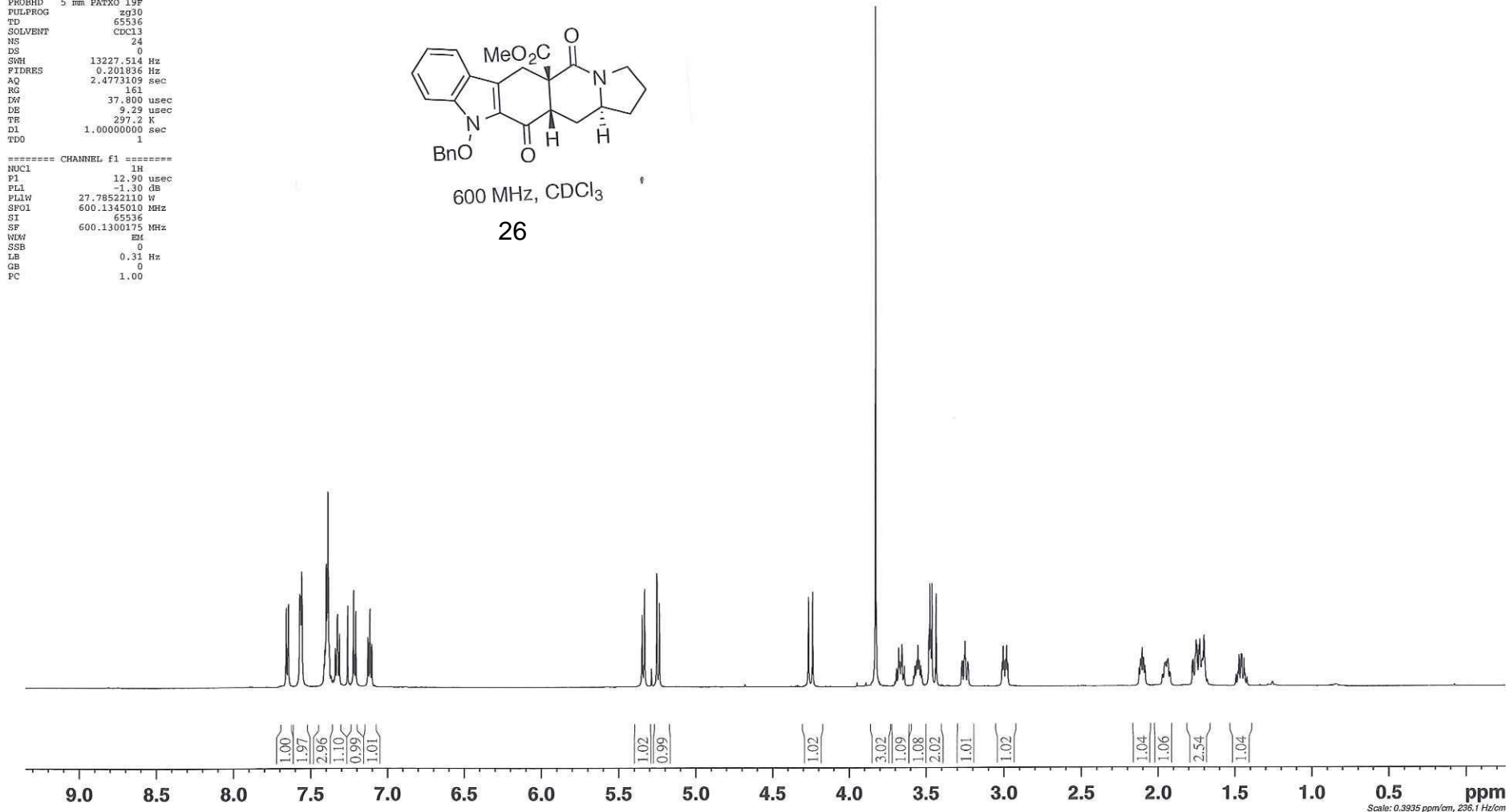
group Danishefsky  
 \* townsens AL-cis-levinson-ketone (10 1) CDC13 24.0C May\_26\_2014\_11:47:30 Bruker AVIII 600MHz RRL1326: janggeum zg30 : 1H 7.500 ppm \*  
 \_ProtonBC CDC13 /opt/users/townsens townsens 8



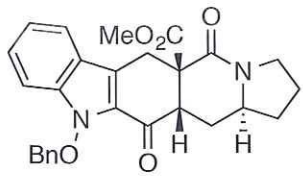
NAME AL-cis-levinson-ketone  
 EXPNO 10  
 PROCNO 1  
 Date\_ 20140526  
 Time 11.47  
 INSTRUM spect  
 PROBHD 5 mm PATXO 19F  
 PULPROG zg30  
 TD 65536  
 SOLVENT CDCl3  
 NS 24  
 DS 0  
 SWH 13227.514 Hz  
 FIDRES 0.201836 Hz  
 AQ 2.4773109 sec  
 RG 161  
 DW 37.800 usec  
 DE 9.29 usec  
 TE 297.2 K  
 D1 1.0000000 sec  
 TDO 1



600 MHz, CDCl<sub>3</sub>  
 26



Scale: 0.3935 ppm/cm, 236.1 Hz/cm



150 MHz, CDCl<sub>3</sub>

26

3

NAME AL-cis-levinson-ketone-c13  
 EXPNO 10  
 PROCNO 1  
 Date\_ 20140526  
 Time 11.52  
 INSTRUM spect  
 PROBHD 5 mm PATXO 19F  
 PULPROG zgpg30  
 TD 134144  
 SOLVENT CDCl3  
 NS 1024  
 DS 0  
 SWH 39062.500 Hz  
 FIDRES 0.291198 Hz  
 AQ 1.7170932 sec  
 RG 2050  
 DW 12.800 usec  
 DE 6.00 usec  
 TE 297.2 K  
 D1 1.10000002 sec  
 D11 0.03000000 sec  
 TD0 1

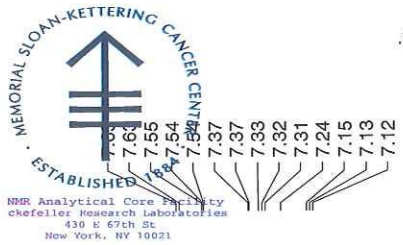
==== CHANNEL f1 =====  
 NUC1 13C  
 P1 12.10 usec  
 PL1 2.50 dB  
 PL1W 60.45660782 W  
 SFO1 150.9194083 MHz

==== CHANNEL f2 =====  
 CPDPRG2 waltz16  
 NUC2 1H  
 PCPD2 80.00 usec  
 PL2 -1.20 dB  
 PL12 14.65 dB  
 PL13 13.94 dB  
 PL2W 27.15275192 W  
 PL12W 0.70601493 W  
 PL13W 0.83140743 W  
 SFO2 600.1327006 MHz  
 SI 131072  
 SF 150.9027852 MHz  
 WDW EM  
 SSB 0  
 LB 1.00 Hz  
 GB 0  
 PC 1.40



Scale: 10.7 ppm/cm, 1614 Hz/cm



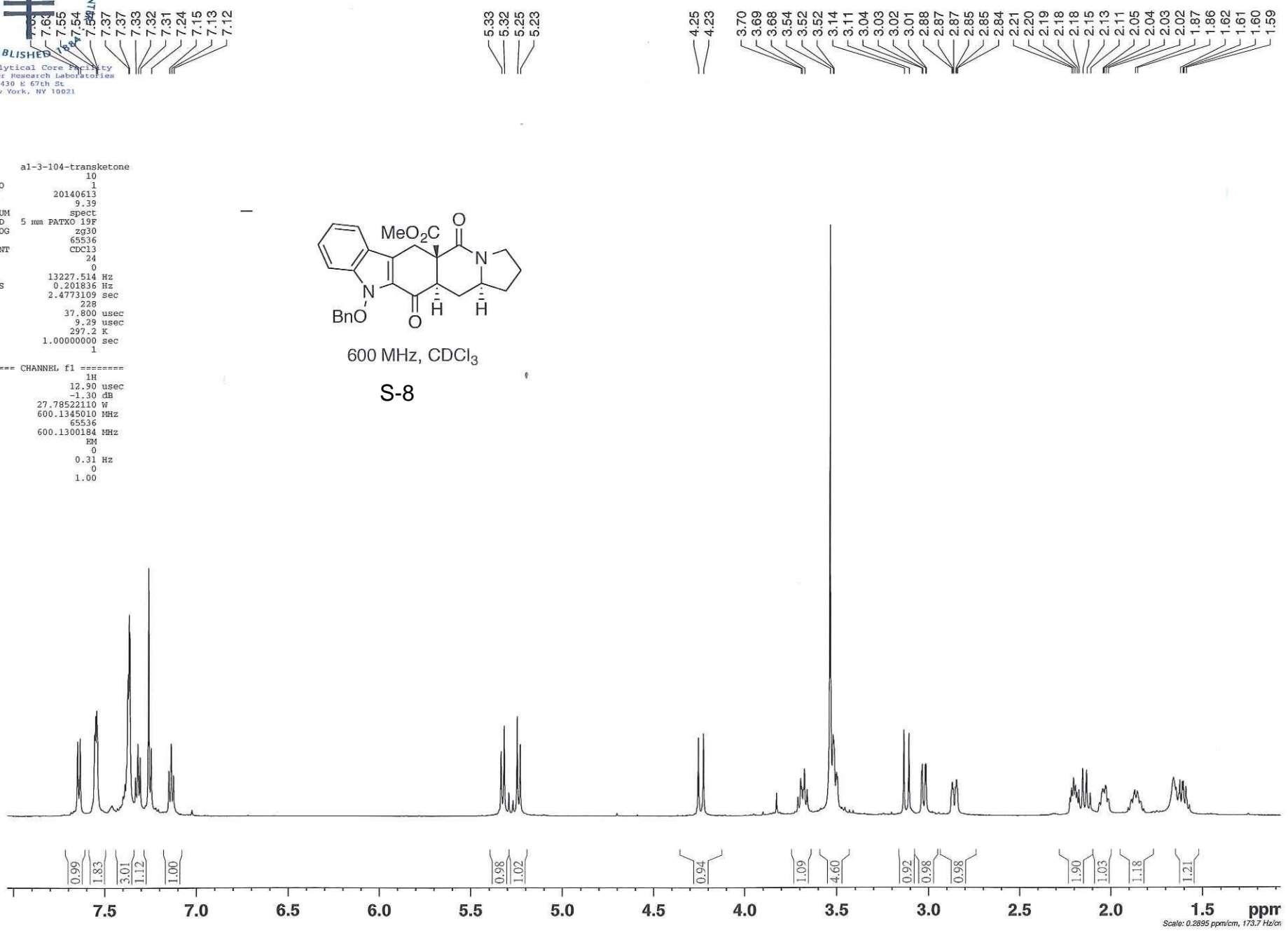
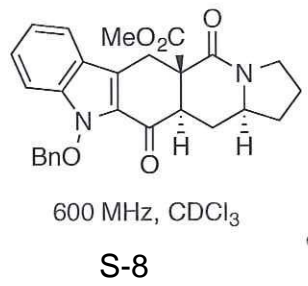


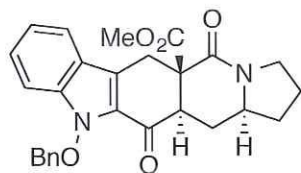
group Danishefsky  
 \*townsens al-3-104-transketone (10 1) CDCI3 24.0C June\_13,2014\_09:39:48 Bruker AVIII 600MHz RRL1326: janggeum zg30 : 1H 7.500 ppm \*  
 \_ProtonBC CDCI3 /opt/users/townsens townsens 15

```

NAME al-3-104-transketone
EXPNO 10
PROCNO 1
Date_ 20140613
Time 9.39
INSTRUM spect
PROBHD 5 mm PATXO 19F
PULPROG zg30
TD 65536
SOLVENT CDCI3
NS 24
DS 0
SWH 13227.514 Hz
FIDRES 0.201836 Hz
AQ 2.4773109 sec
RG 228
DW 37.800 usec
DE 9.29 usec
TE 297.2 K
D1 1.0000000 sec
TDO 1

===== CHANNEL f1 =====
NUC1 1H
P1 12.90 usec
PL1 -1.30 dB
PL1W 27.78522110 W
SFO1 600.1345010 MHz
SI 65536
SF 600.1300184 MHz
WDW EM
SSB 0
LB 0.31 Hz
GB 0
EC 1.00
  
```





150 MHz, CDCl<sub>3</sub>

S-8

NAME al-3-104-transketone-c13  
EXPNO 10  
PROCNO 1  
Date\_ 20140613  
Time 9.44  
INSTRUM spect  
PROBHD 5 mm PATXO 19F  
PULPROG zgpg30  
TD 134144  
SOLVENT CDCl3  
NS 1024  
DS 0  
SWH 39062.500 Hz  
FIDRES 0.291198 Hz  
AQ 1.7170932 sec  
RG 2050  
DW 12.800 usec  
DE 6.00 usec  
TE 297.2 K  
D1 1.10000002 sec  
D11 0.03000000 sec  
TD0 1

===== CHANNEL f1 =====  
NUC1 13C  
P1 12.10 usec  
PL1 2.50 dB  
PL1W 60.45660782 W  
SFO1 150.9194083 MHz

===== CHANNEL f2 =====  
CPDPRG2 waltz16  
NUC2 1H  
PCPD2 80.00 usec  
PL2 -1.20 dB  
PL12 14.65 dB  
PL13 13.94 dB  
PL2W 27.15275192 W  
PL12W 0.70601493 W  
PL13W 0.83140743 W  
SFO2 600.1327006 MHz  
SI 131072  
SF 150.9027914 MHz  
WDW EM  
SSB 0  
LB 1.00 Hz  
GB 0  
PC 1.40





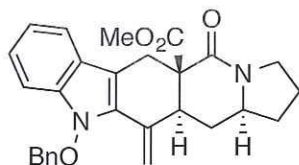
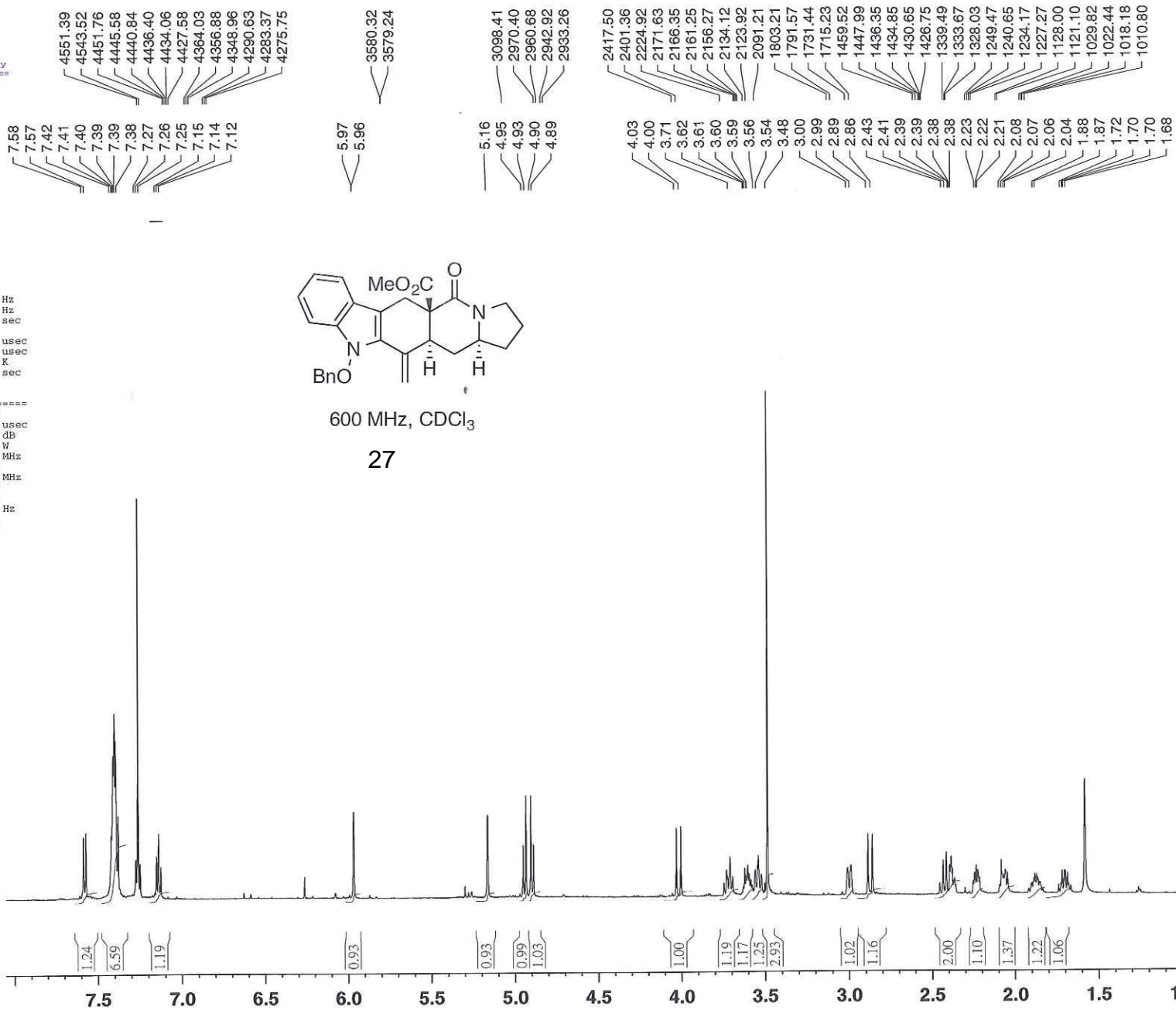


MEMORIAL SLOAN-KETTERING CANCER CENTER  
ESTABLISHED 1884  
NMR Analytical Core Facility  
Chefeller Research Laboratories  
430 E 67th St  
New York, NY 10021

group Danishefsky  
\* levinsoa AL-3-140 (10 1) CDC13 24.0C July\_17\_2014\_17:59:55 Bruker AVIII 600MHz RRL1326: janggeum zg30 : 1H 7.500 ppm \*  
\_ProtonBC CDC13 /opt/users/levinsoa levinsoa 9

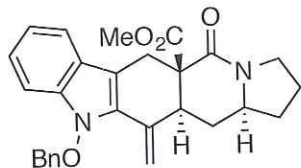
NAME AL-3-140  
EXPNO 10  
PROCNO 1  
Date\_ 20140717  
Time 18.00  
INSTRUM spect  
PROBHD 5 mm PATXO 13P  
PULPROG zg30  
TD 65536  
SOLVENT CDC13  
NS 24  
DS 0  
SWH 13227.514 Hz  
FIDRES 0.201836 Hz  
AQ 2.4773109 sec  
RG 322  
DW 37.800 usec  
DE 9.29 usec  
TE 297.2 K  
D1 1.00000000 sec  
TD0 1

===== CHANNEL f1 =====  
NUC1 1H  
P1 12.90 usec  
PL1 -1.30 dB  
PL1W 27.78522110 W  
SFO1 600.1345010 MHz  
SI 65536  
SF 600.1300176 MHz  
WDW EM  
SSB 0  
LB 0.31 Hz  
GB 0  
PC 1.00



600 MHz, CDCl<sub>3</sub>

27



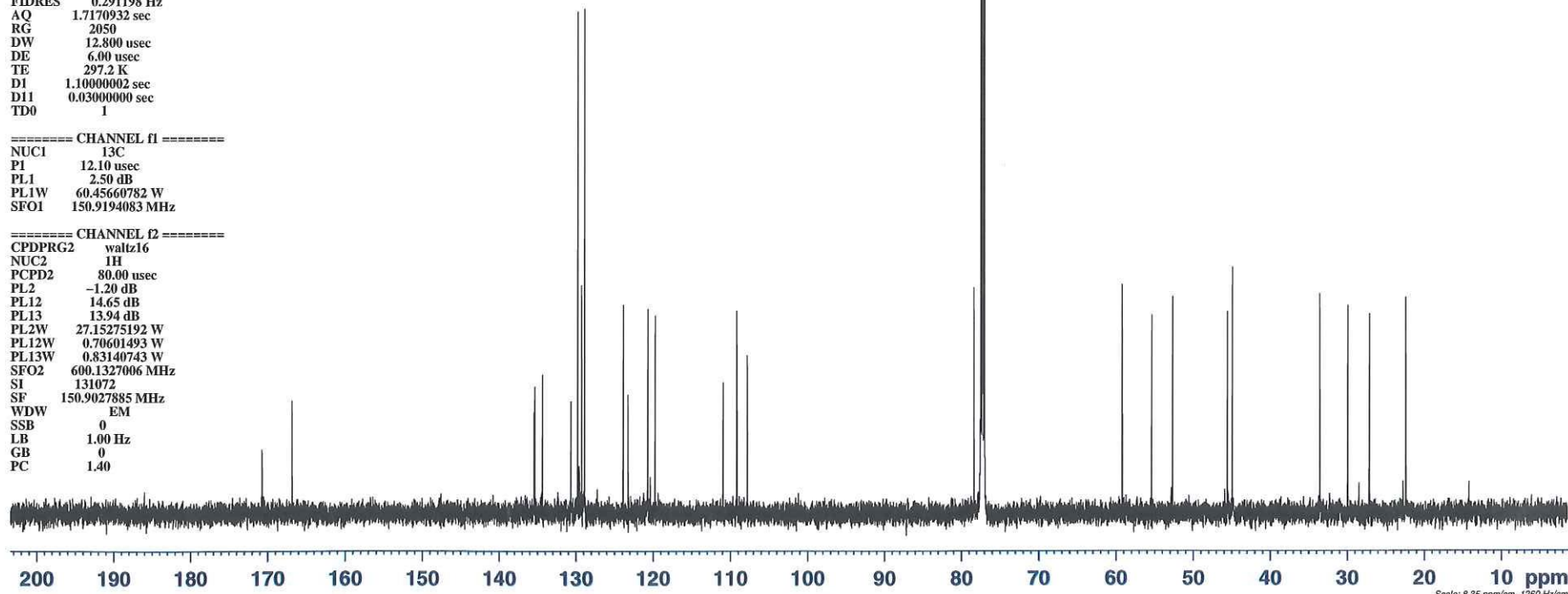
150 MHz, CDCl<sub>3</sub>

27

NAME AL-3-140-c13  
EXPNO 10  
PROCNO 1  
Date\_ 20140717  
Time 22.53  
INSTRUM spect  
PROBHD 5 mm PATXO 19F  
PULPROG zgpg30  
TD 134144  
SOLVENT CDCl3  
NS 3500  
DS 0  
SWH 39062.500 Hz  
FIDRES 0.291198 Hz  
AQ 1.7170932 sec  
RG 2050  
DW 12.800 usec  
DE 6.00 usec  
TE 297.2 K  
D1 1.1000002 sec  
D11 0.03000000 sec  
TD0 1

===== CHANNEL f1 =====  
NUC1 13C  
PI 12.10 usec  
PL1 2.50 dB  
PL1W 60.45660782 W  
SFO1 150.9194083 MHz

===== CHANNEL f2 =====  
CPDPRG2 waltz16  
NUC2 1H  
PCPD2 80.00 usec  
PL2 -1.20 dB  
PL12 14.65 dB  
PL13 13.94 dB  
PL2W 27.15275192 W  
PL12W 0.70601493 W  
PL13W 0.83140743 W  
SFO2 600.1327006 MHz  
SI 131072  
SF 150.9027885 MHz  
WDW EM  
SSB 0  
LB 1.00 Hz  
GB 0  
PC 1.40



Scale: 8.35 ppm/cm, 1260 Hz/cm



MSK Analytical Core Facility  
 Rockefeller Research Laboratories  
 430 E 67th St  
 New York, NY 10021

Current Data Parameters  
 NAME AL-3-107-azide-2  
 EXPNO 1  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20140615  
 Time 7.26  
 INSTRUM spect  
 PROBHD 5 mm QNP 1H/13  
 PULPROG zg30  
 TD 32768  
 SOLVENT CDC13  
 NS 17  
 DS 0  
 SWH 10964.912 Hz  
 FIDRES 0.334623 Hz  
 AQ 1.4942708 sec  
 RG 812.7  
 DW 45.600 usec  
 DE 6.00 usec  
 TE 297.2 K  
 D1 1.00000000 sec  
 TD0 1

===== CHANNEL f1 =====  
 NUC1 1H  
 P1 14.00 usec  
 PL1 -1.00 dB  
 SFO1 500.1340010 MHz

F2 - Processing parameters  
 SI 32768  
 SF 500.1300136 MHz  
 WDW EM  
 SSB 0  
 LB 0.30 Hz  
 GB 0  
 PC 1.00

7.59  
7.58  
7.41  
7.30  
7.28  
7.26  
7.17  
7.16  
7.14

6.03

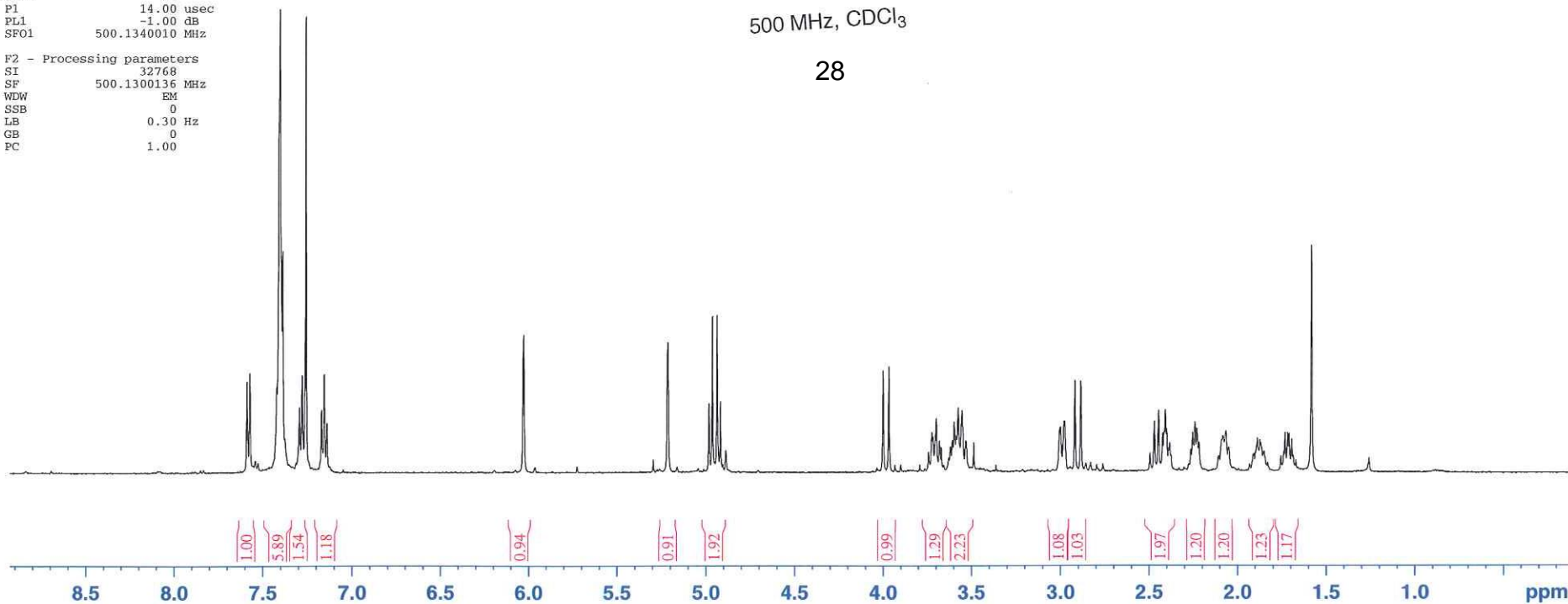
5.22  
4.99  
4.97  
4.94  
4.92

Protons  
4.00  
3.96  
3.72  
3.71  
3.70  
3.68  
3.59  
3.57  
3.55  
3.00  
2.98  
2.92  
2.89  
2.50  
2.47  
2.45  
2.43  
2.42  
2.41  
2.40  
2.39  
2.38  
2.25  
2.24  
2.23  
2.08  
2.07  
1.89  
1.87  
1.87  
1.86  
1.85  
1.73  
1.72  
1.71  
1.69



500 MHz, CDCl<sub>3</sub>

28





MSK Analytical Core Facility  
Rockefeller Research Laboratories  
430 E 71st St  
New York, NY 10021

178.33

165.93

Carbon  
135.28  
134.69  
134.18  
130.51  
129.73  
129.25  
128.78  
124.05  
122.91  
120.74  
119.60  
110.02  
109.58  
108.98

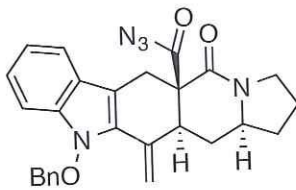
78.51

59.15  
56.30

45.67  
44.96

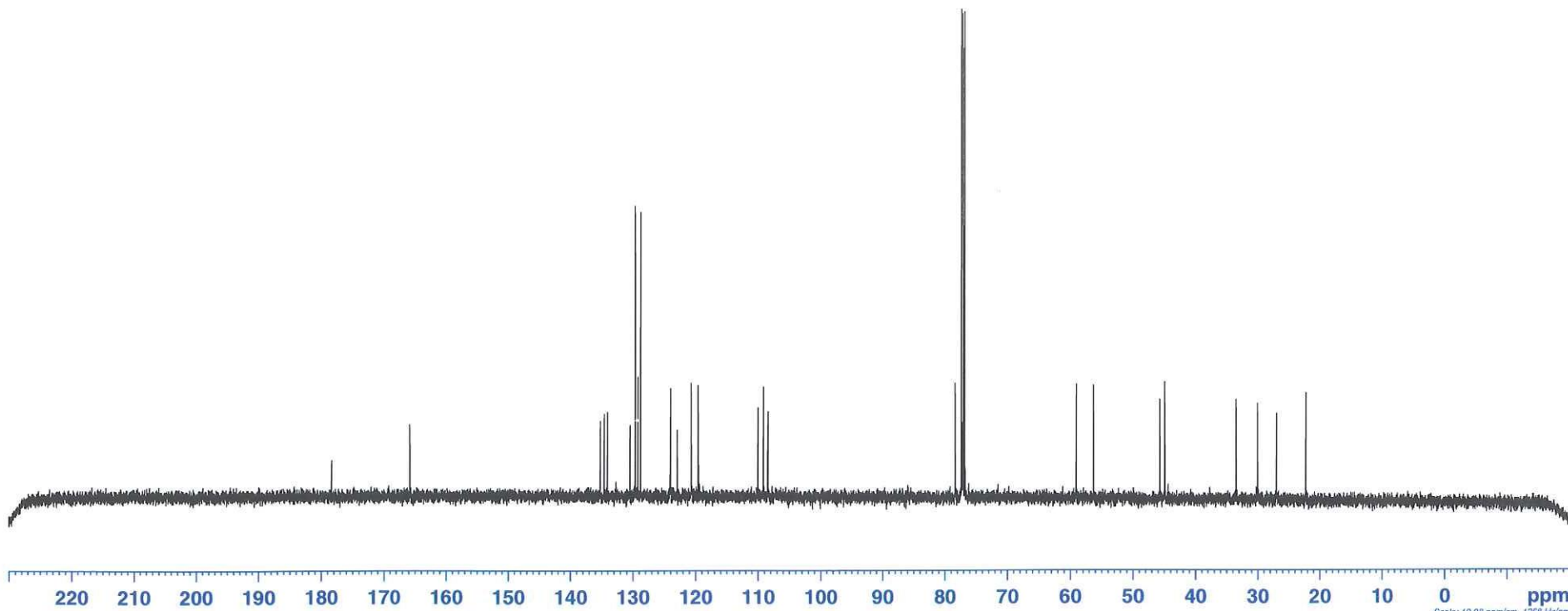
33.50  
29.99

26.96  
22.27



125 MHz, CDCl<sub>3</sub>

28



Scale: 10.08 ppm/cm, 1268 Hz/cm



NMR Analytical Core Facility  
 Rockefeller Research Laboratories  
 430 E 67th St  
 New York, NY 10021

Current Data Parameters  
 NAME al-3-141-carbamate-repurified-2  
 EXPTNO 1  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20140721  
 Time 11.16  
 INSTRUM spect  
 PROBHD 5 mm QNP 1H/13  
 PULPROG zg30  
 TD 32768  
 SOLVENT CDCl3  
 NS 24  
 DS 0  
 SFO 10964.912 Hz  
 FIDRES 0.334623 Hz  
 AQ 1.4942708 sec  
 RG 974.7  
 DW 45.600 usec  
 DE 6.00 usec  
 TE 297.2 F  
 D1 1.00000000 sec  
 TDO 1

===== CHANNEL f1 =====  
 NUCL1 1H  
 P1 14.00 usec  
 PL1 -1.00 dB  
 SFO1 500.1340010 MHz

F2 - Processing parameters  
 SI 32768  
 SF 500.1300139 MHz  
 WDW EM  
 SSB 0  
 LB 0.30 Hz  
 GB 0  
 PC 1.00

7.52  
7.50  
7.45  
7.44  
7.42  
7.41  
7.30  
7.29  
7.27  
7.16  
7.15  
7.13

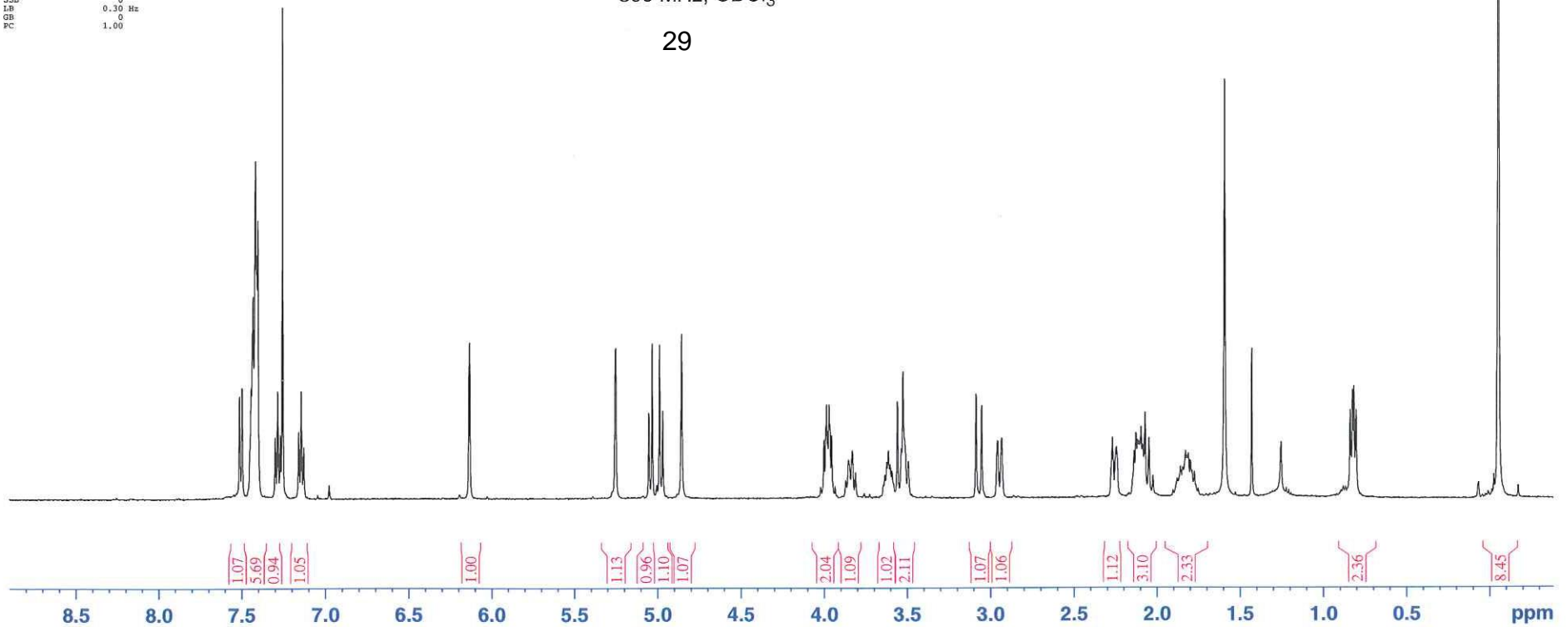
6.13

5.26  
5.06  
5.04  
4.99  
4.97  
4.86  
4.00  
3.99  
3.97  
3.96  
3.87  
3.85  
3.83  
3.81  
3.62  
3.61  
3.56  
3.53  
3.52  
3.49  
3.08  
3.05  
2.96  
2.93  
2.27  
2.25  
2.14  
2.13  
2.12  
2.11  
2.10  
2.09  
2.08  
2.05  
2.03  
1.88  
1.86  
1.85  
1.83  
1.82  
1.81  
1.80  
1.79  
1.78  
0.84  
0.82  
0.80



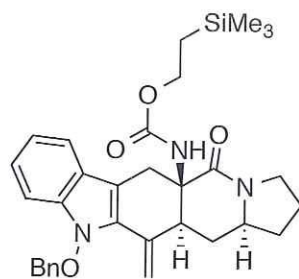
500 MHz, CDCl<sub>3</sub>

29



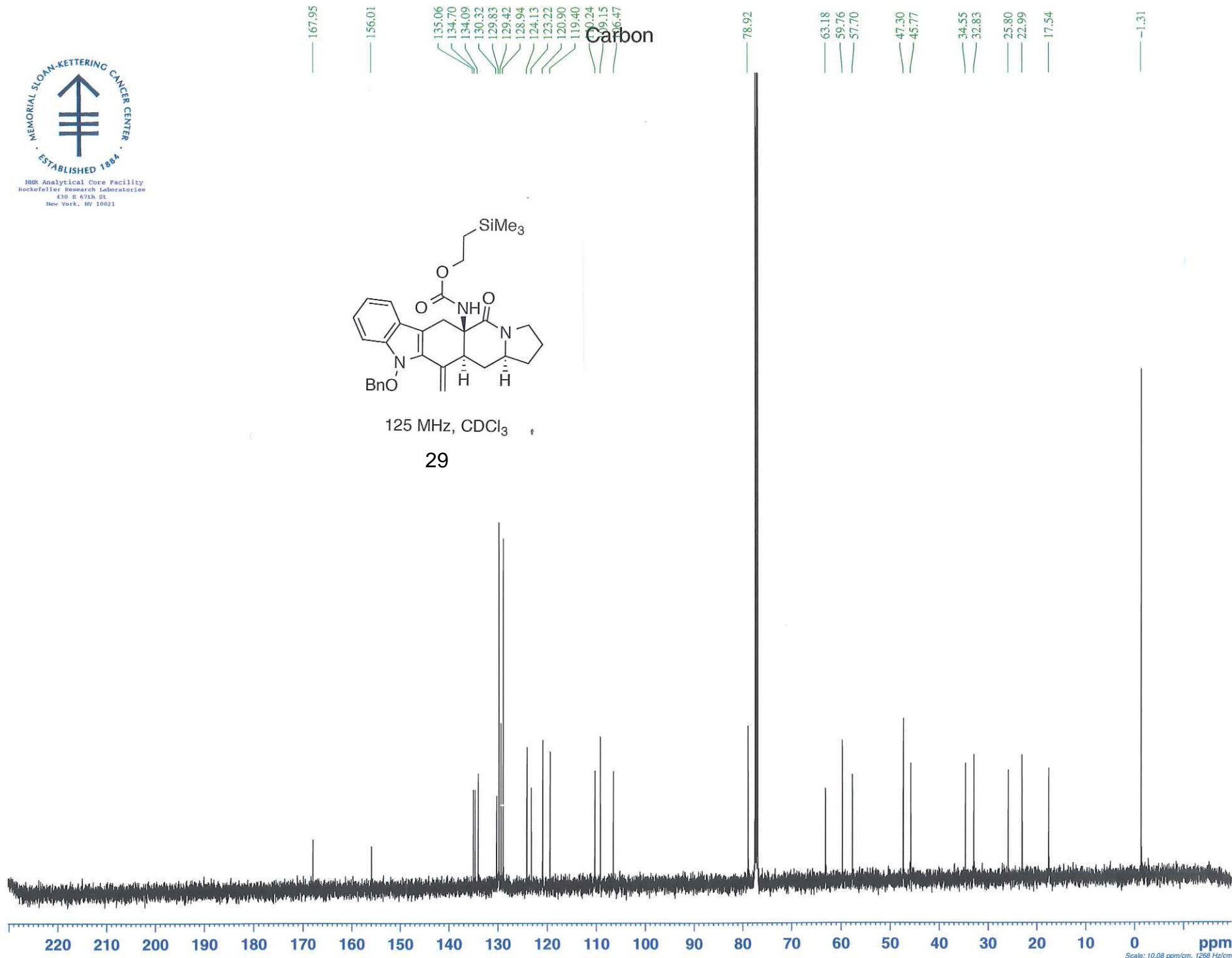


MSK Analytical Core Facility  
Rockefeller Research Laboratories  
430 E 67th St.  
New York, NY 10021



125 MHz, CDCl<sub>3</sub>

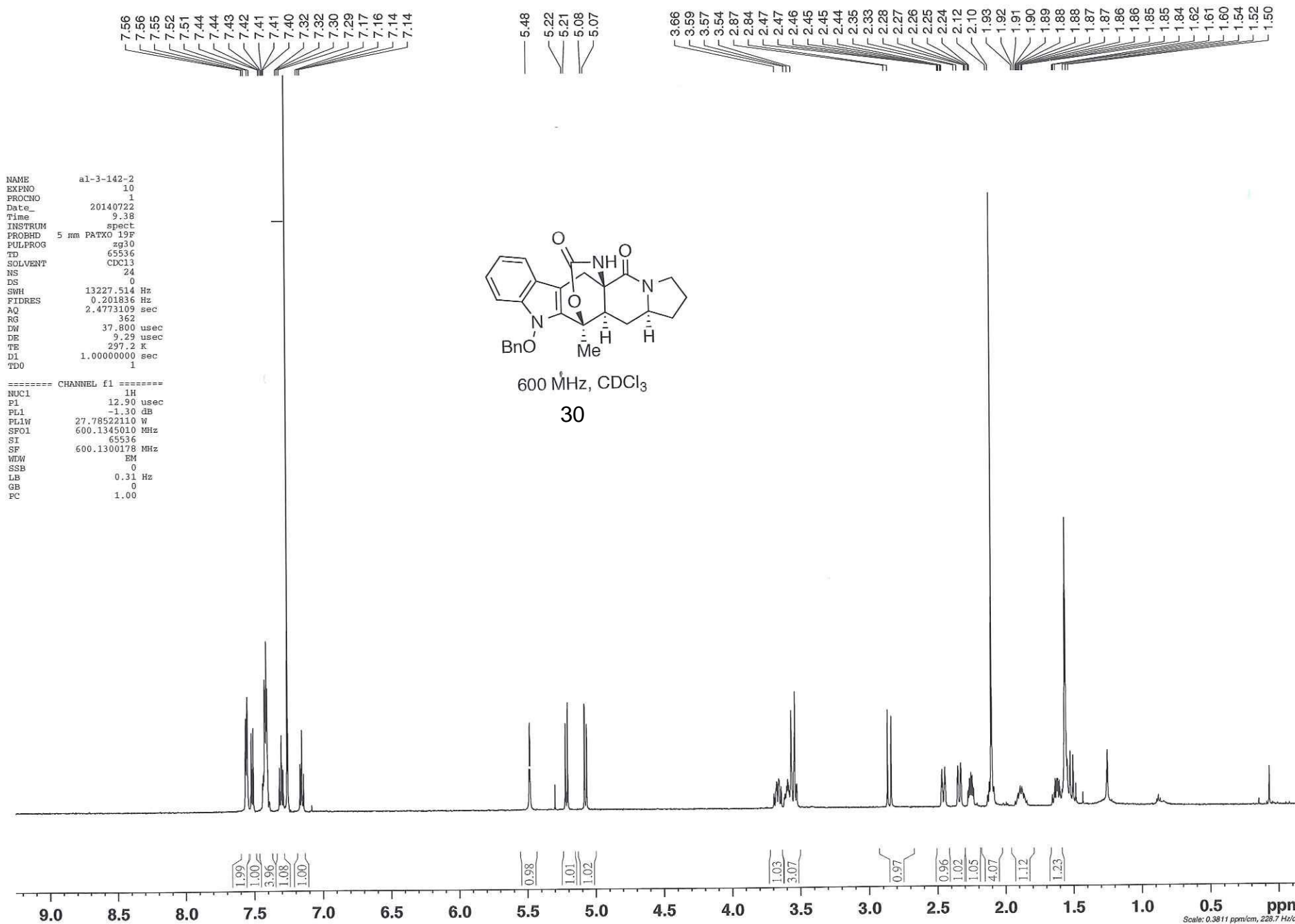
29



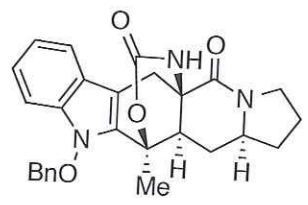
Scale: 10.08 ppm/cm, 1268 Hz/cm



group Danishefsky  
 \*. levinsoa al-3-142-2 (10 1) CDCl3 24.0C July\_22,2014\_09:37:25 Bruker AVIII 600MHz RRL1326: janggeum zg30 : 1H 7.500 ppm \*  
 \_ProtonBC CDCl3 /opt/users/levinsoa levinsoa 34

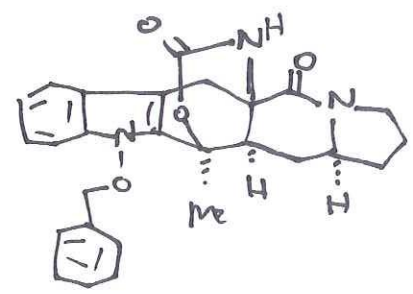


167.62  
 152.37  
 134.71  
 134.16  
 130.63  
 130.01  
 129.31  
 128.87  
 124.37  
 122.14  
 120.92  
 119.48  
 109.55  
 107.42  
 80.13  
 75.41  
 58.46  
 56.79  
 45.67  
 43.06  
 33.72  
 33.57  
 25.22  
 22.52  
 20.17



150 MHz, CDCl<sub>3</sub>

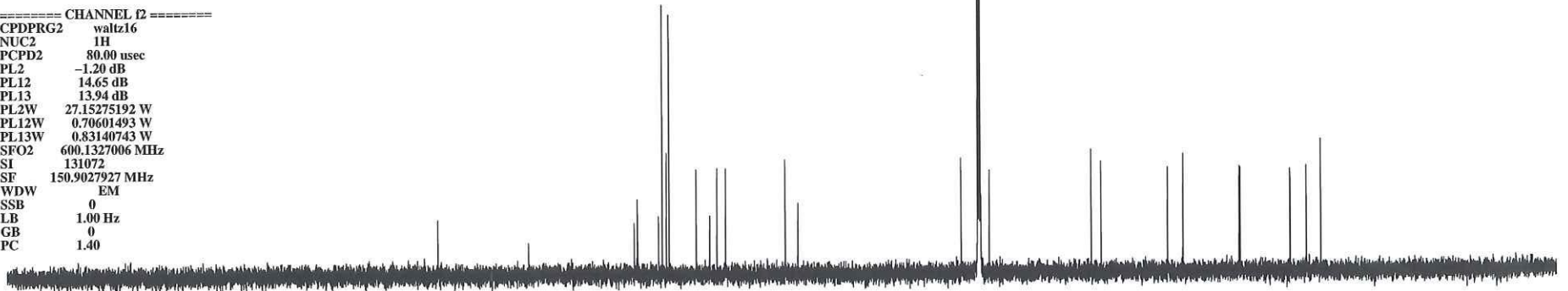
30



NAME al-3-142-c13  
 EXPNO 10  
 PROCNO 1  
 Date\_ 20140721  
 Time 17.35  
 INSTRUM spect  
 PROBHD 5 mm PATXO 19F  
 PULPROG zgpg30  
 TD 134144  
 SOLVENT CDCl3  
 NS 3000  
 DS 0  
 SWH 39062.500 Hz  
 FIDRES 0.291198 Hz  
 AQ 1.7170932 sec  
 RG 2050  
 DW 12.800 usec  
 DE 6.00 usec  
 TE 297.2 K  
 DI 1.1000002 sec  
 D11 0.03000000 sec  
 TD0 1

==== CHANNEL f1 =====  
 NUC1 13C  
 P1 12.10 usec  
 PL1 2.50 dB  
 PL1W 60.45660782 W  
 SFO1 150.9194083 MHz

==== CHANNEL f2 =====  
 CPDPRG2 waltz16  
 NUC2 1H  
 PCPD2 80.00 usec  
 PL2 -1.20 dB  
 PL12 14.65 dB  
 PL13 13.94 dB  
 PL2W 27.15275192 W  
 PL12W 0.70601493 W  
 PL13W 0.83140743 W  
 SFO2 600.1327006 MHz  
 SI 131072  
 SF 150.9027927 MHz  
 WDW EM  
 SSB 0  
 LB 1.00 Hz  
 GB 0  
 PC 1.40



230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm  
 Scale: 10.7 ppm/cm, 1614 Hz/cm





NMR Analytical Core Facility  
 Rockefeller Research Laboratories  
 430 E 67th St  
 New York, NY 10021

Current Data Parameters  
 NAME AL-3-064  
 EXPNO 1  
 PROCNO 1

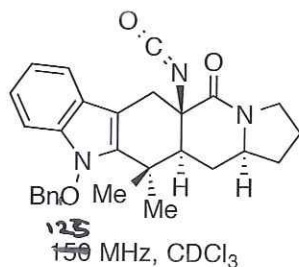
F2 - Acquisition Parameters  
 Date\_ 20140514  
 Time 10.25  
 INSTRUM spect  
 PROBHD 5 mm QNP 1H/13  
 PULPROG zg30  
 TD 32768  
 SOLVENT CDCl3  
 NS 24  
 DS 0  
 SWH 10964.912 Hz  
 FIDRES 0.334623 Hz  
 AQ 1.4942708 sec  
 RG 812.7  
 DW 45.600 usec  
 DE 6.00 usec  
 TE 297.2 K  
 D1 1.00000000 sec  
 TD0 1

==== CHANNEL f1 =====  
 NUC1 1H  
 P1 14.00 usec  
 PL1 -1.00 dB  
 SFO1 500.1340010 MHz

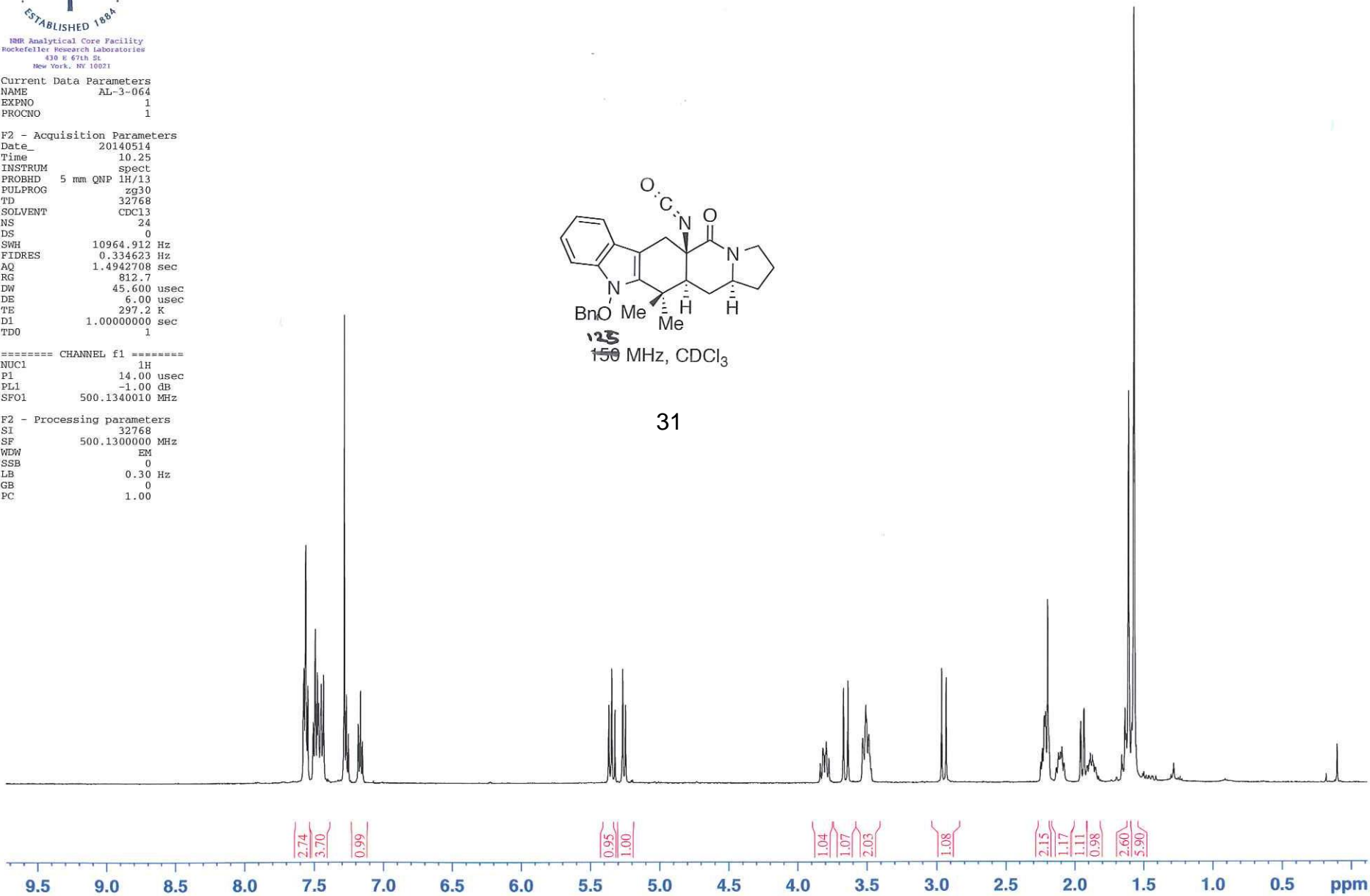
F2 - Processing parameters  
 SI 32768  
 SF 500.1300000 MHz  
 WDW EM  
 SSB 0  
 LB 0.30 Hz  
 GB 0  
 PC 1.00

7.58  
7.57  
7.55  
7.51  
7.50  
7.48  
7.47  
7.46  
7.46  
7.45  
7.44  
7.29  
7.27  
7.26  
7.18  
7.17  
7.15

5.37  
5.35  
5.33  
5.27  
5.25  
5.24  
3.84  
3.82  
3.81  
3.79  
3.77  
3.67  
3.63  
3.53  
3.51  
3.50  
3.48  
3.47  
3.47  
2.96  
2.93  
2.25  
2.24  
2.22  
2.21  
2.20  
2.13  
2.12  
2.11  
2.10  
2.08  
1.96  
1.93  
1.91  
1.91  
1.90  
1.89  
1.89  
1.87  
1.87  
1.86  
1.85  
1.85  
1.66  
1.65  
1.64  
1.63  
1.61  
1.59  
1.57  
1.56  
1.51  
1.50



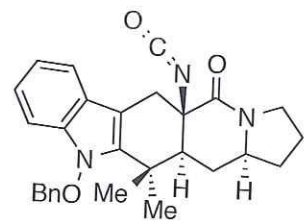
31



NAME al-3-064-c13  
 EXPNO 10  
 PROCNO 1  
 Date\_ 20140514  
 Time 18.30  
 INSTRUM spect  
 PROBHD 5 mm PATXO 19F  
 PULPROG zgpg30  
 TD 134144  
 SOLVENT CDC13  
 NS 2500  
 DS 0  
 SWH 39062.500 Hz  
 FIDRES 0.291198 Hz  
 AQ 1.7170932 sec  
 RG 2050  
 DW 12.800 usec  
 DE 6.00 usec  
 TE 297.2 K  
 D1 1.1000002 sec  
 D11 0.03000000 sec  
 TD0 1

===== CHANNEL f1 =====  
 NUC1 13C  
 P1 12.10 usec  
 PL1 2.50 dB  
 PL1W 60.45660782 W  
 SFO1 150.9194083 MHz

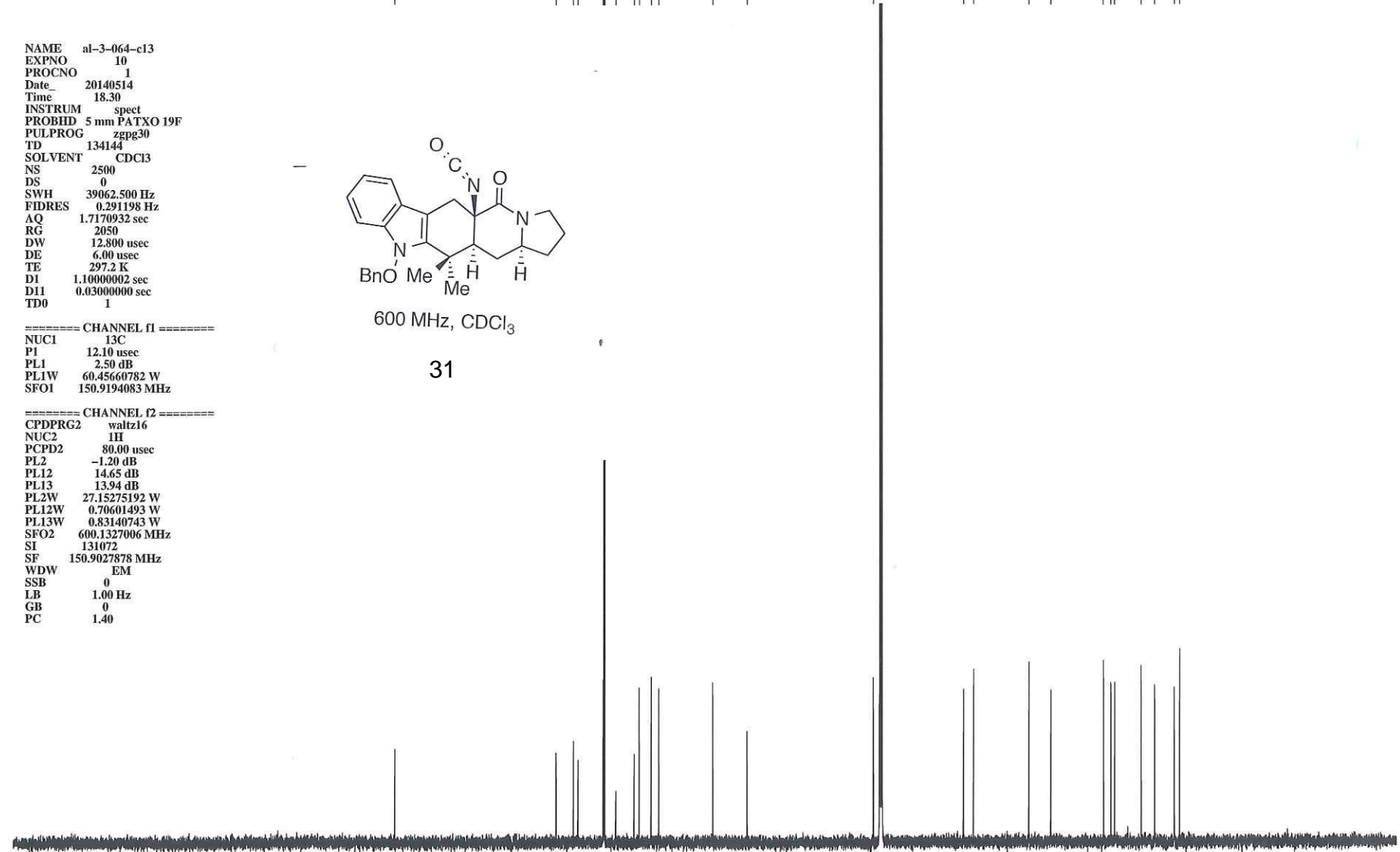
===== CHANNEL f2 =====  
 CPDPRG2 waltz16  
 NUC2 1H  
 PCPD2 80.00 usec  
 PL2 -1.20 dB  
 PL12 14.65 dB  
 PL13 13.94 dB  
 PL2W 27.15275192 W  
 PL12W 0.70601493 W  
 PL13W 0.83140743 W  
 SFO2 600.1327006 MHz  
 SI 131072  
 SF 150.9027878 MHz  
 WDW EM  
 SSB 0  
 LB 1.00 Hz  
 GB 0  
 PC 1.40



600 MHz, CDCl<sub>3</sub>

31

168.30  
 137.88  
 134.61  
 133.80  
 129.12  
 128.98  
 128.79  
 126.78  
 123.38  
 122.41  
 120.20  
 118.83  
 108.75  
 102.34  
 78.55  
 61.76  
 59.88  
 49.54  
 45.45  
 35.63  
 34.23  
 33.53  
 28.59  
 26.08  
 22.41  
 21.40



230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm  
 Scale: 10.7 ppm/cm, 1614 Hz/cm



MSK Analytical Core Facility  
 Rockefeller Research Laboratories  
 430 E 67th St  
 New York, NY 10021

Current Data Parameters  
 NAME al-3-120-2  
 EXPNO 1  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20140623  
 Time 11.06  
 INSTRUM spect  
 PROBHD 5 mm QNP 1H/13  
 PULPROG zg30  
 TD 32768  
 SOLVENT CDCl3  
 NS 8  
 DS 0  
 SWH 10964.912 Hz  
 FIDRES 0.334623 Hz  
 AQ 1.4942708 sec  
 RG 456.1  
 DW 45.600 usec  
 DE 6.00 usec  
 TE 297.2 K  
 D1 1.00000000 sec  
 TDO 1

===== CHANNEL f1 =====  
 NUC1 1H  
 P1 14.00 usec  
 PL1 -1.00 dB  
 SFO1 500.1340010 MHz

F2 - Processing parameters  
 SI 32768  
 SF 500.1300133 MHz  
 WDW EM  
 SSB 0  
 LB 0.30 Hz  
 GB 0  
 PC 1.00

8.15  
 7.49  
 7.48  
 7.36  
 7.35  
 7.26  
 7.20  
 7.18  
 7.17  
 7.13  
 7.12  
 7.10

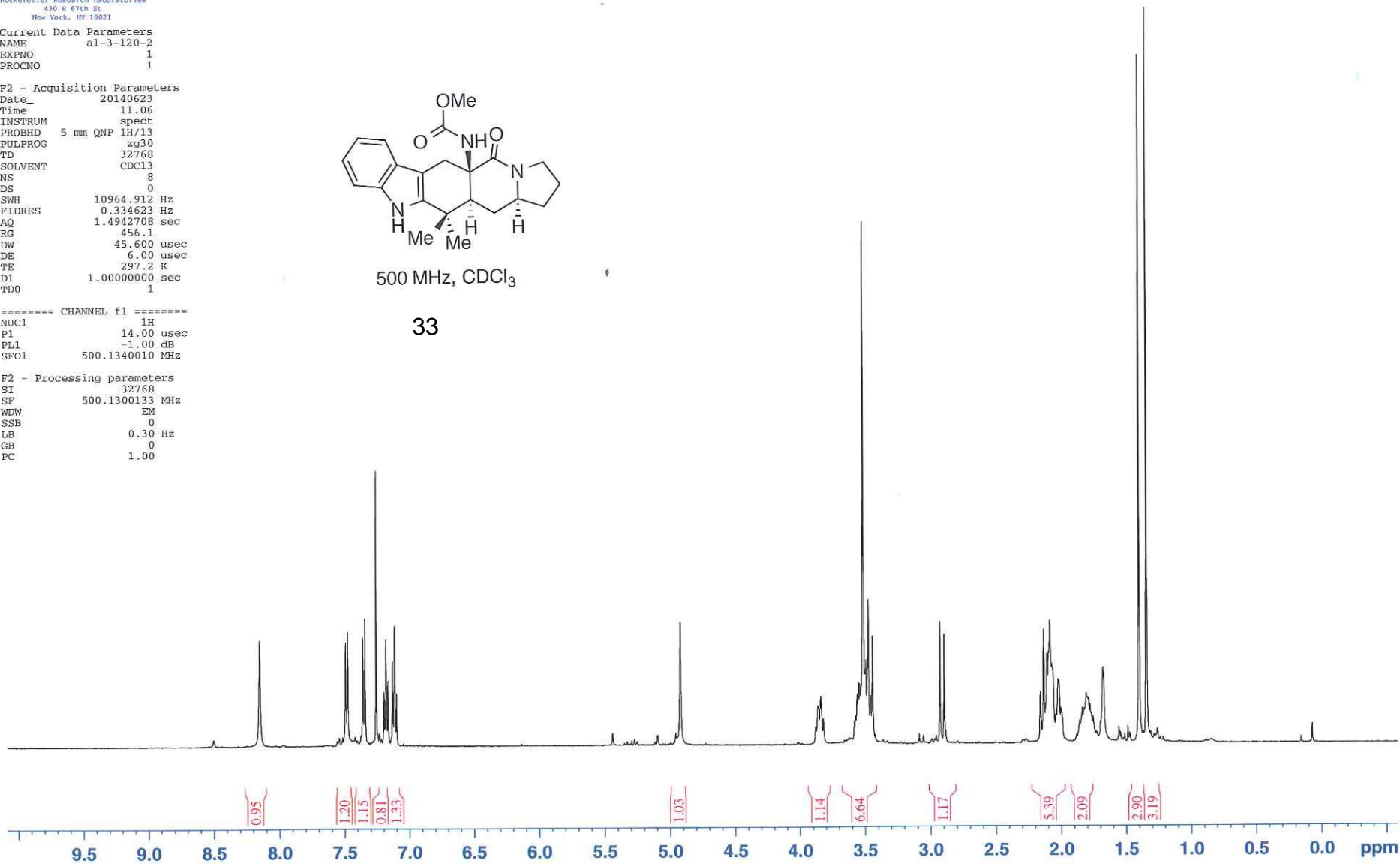
Proton24

4.92  
 3.86  
 3.84  
 3.52  
 3.50  
 3.49  
 3.48  
 3.44  
 2.93  
 2.90  
 2.13  
 2.09  
 1.81  
 1.79  
 1.40  
 1.34



500 MHz, CDCl<sub>3</sub>

33





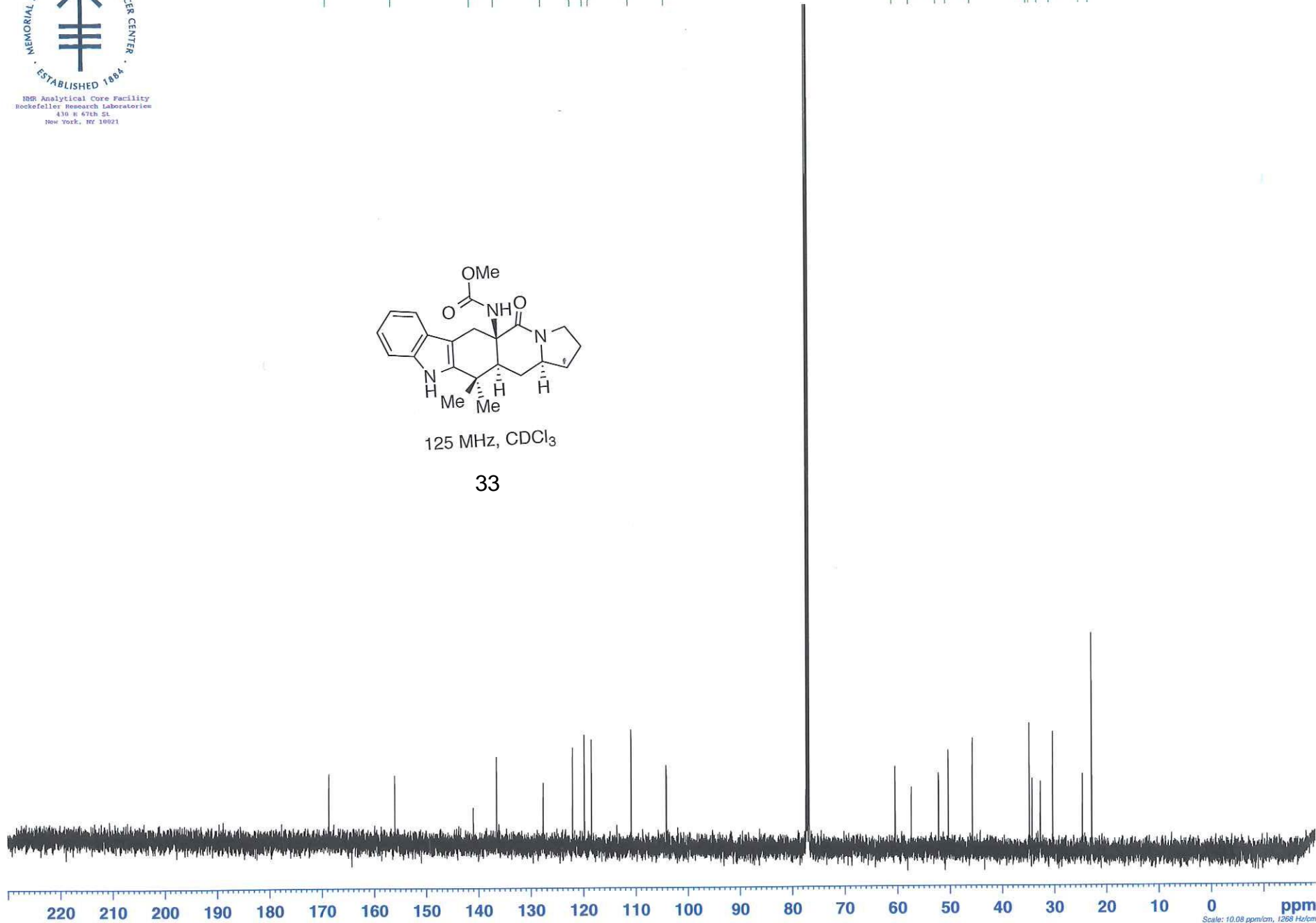
MSR Analytical Core Facility  
Rockefeller Research Laboratories  
430 R 67th St  
New York, NY 10021

168.78  
156.16  
141.07  
136.56  
127.61  
122.04  
119.71  
118.51  
110.6  
104  
Carbon  
60.47  
57.34  
52.13  
50.26  
45.60  
34.79  
34.24  
32.65  
30.29  
24.64  
22.83



125 MHz, CDCl<sub>3</sub>

33



Scale: 10.08 ppm/cm, 1268 Hz/cm



NMR Analytical Core Facility  
Rockefeller Research Laboratories  
430 E 67th St  
New York, NY 10021

Current Data Parameters  
NAME al-3-121  
EXPNO 1  
PROCNO 1

F2 - Acquisition Parameters  
Date\_ 20140623  
Time 18.34  
INSTRUM spect  
PROBHD 5 mm QNP 1H/13  
PULPROG zg30  
TD 32768  
SOLVENT CDCl3  
NS 24  
DS 0  
SWH 10964.912 Hz  
FIDRES 0.334623 Hz  
AQ 1.4942708 sec  
RG 456.1  
DW 45.600 usec  
DE 6.00 usec  
TE 297.2 K  
D1 1.00000000 sec  
TD0 1

----- CHANNEL f1 -----  
NUC1 1H  
P1 14.00 usec  
PL1 -1.00 dB  
SFO1 500.1340010 MHz

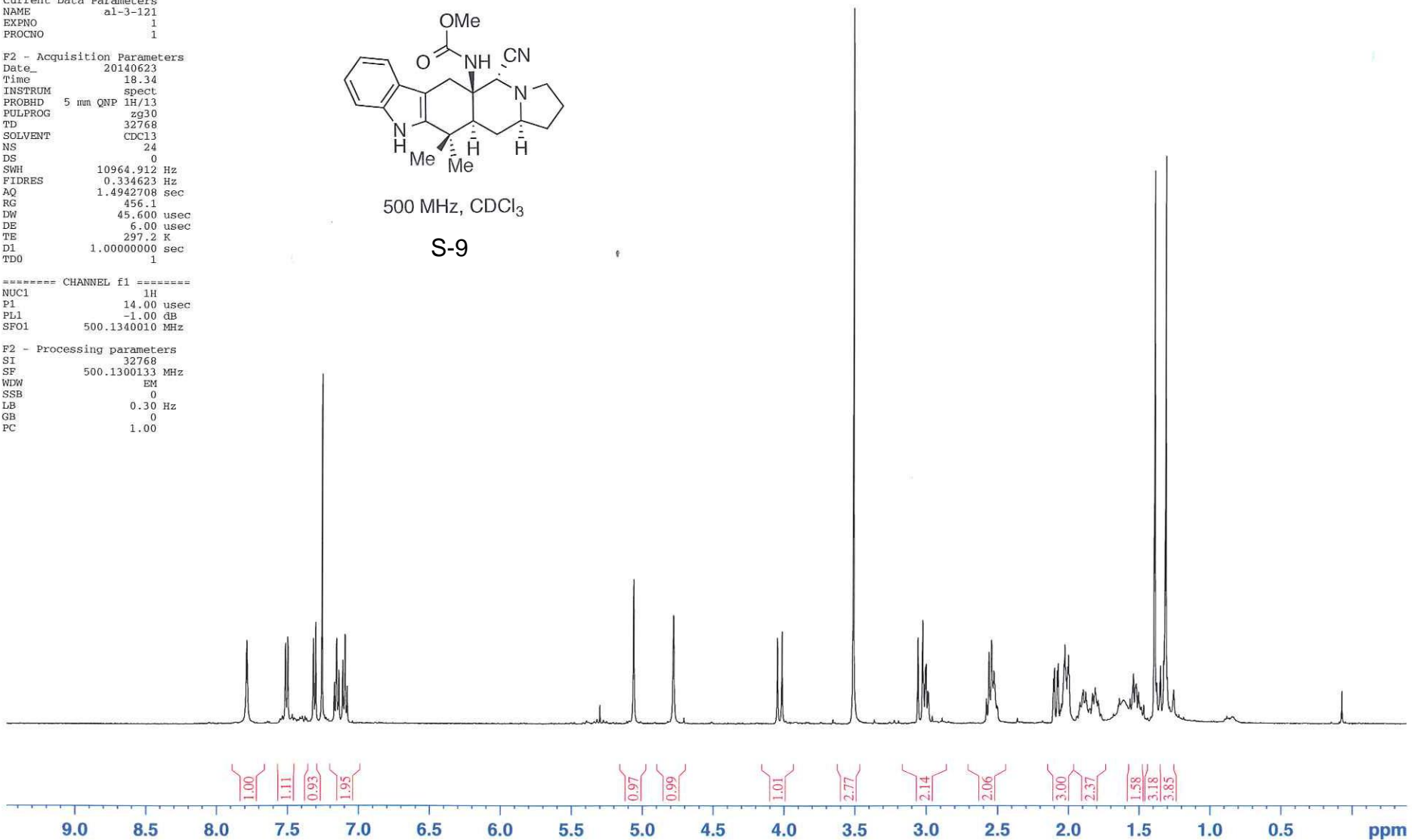
F2 - Processing parameters  
SI 32768  
SF 500.1300133 MHz  
WDW EM  
SSB 0  
LB 0.30 Hz  
GB 0  
PC 1.00



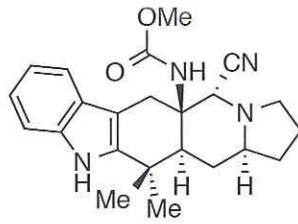
500 MHz, CDCl<sub>3</sub>

S-9

7.79 7.52 7.50 7.32 7.31 7.26 7.17 7.16 7.14 7.11 7.10 7.08  
5.06 4.78 Proton24 4.05 4.02  
3.51 3.06 3.02 3.01 3.00 2.56 2.54 2.52 2.10 2.10 2.08 2.07 2.02 2.02 2.00 1.90 1.89 1.88 1.83 1.82 1.81 1.54 1.53 1.52 1.39 1.32



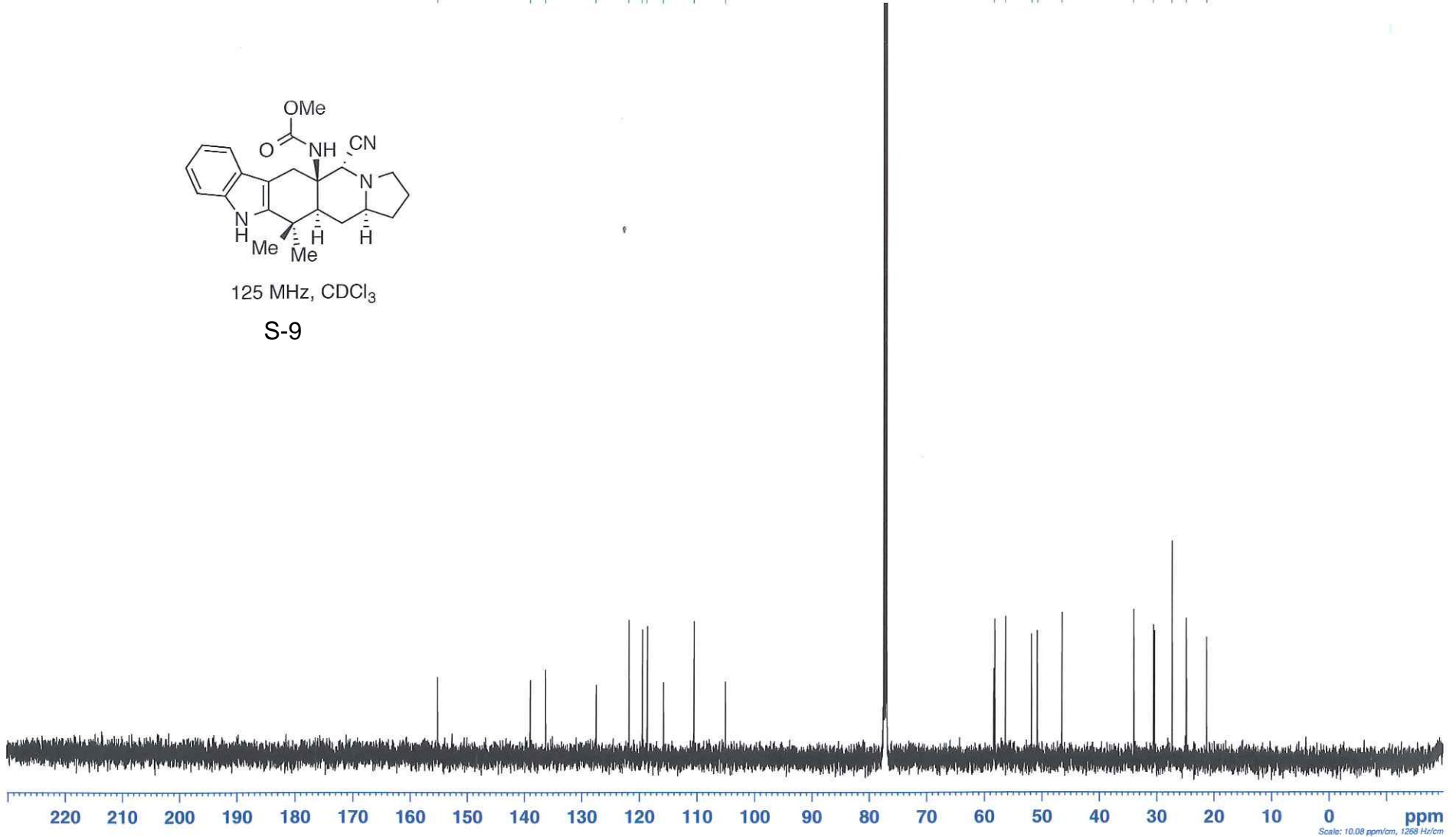
# Carbon



125 MHz, CDCl<sub>3</sub>

S-9

155.32	19532.17								
139.01	17481.24								
136.39	17152.32								
127.62	16049.46								
121.93	15333.57								
119.62	15043.35								
118.78	14936.93								
115.93	14578.99								
110.62	13911.46								
105.16	13224.60								
58.42	7347.22								
56.49	7104.17								
51.85	6520.83								
50.86	6395.84								
46.55	5854.16								
34.07	4284.72								
30.65	3854.16								
27.39	3444.44								
24.85	3125.01								
21.32	2680.55								







NMR Analytical Core Facility  
 Rockefeller Research Laboratories  
 430 E 71st St  
 New York, NY 10021

Current Data Parameters  
 NAME al-3-122-2  
 EXPNO 1  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20140623  
 Time 21.37  
 INSTRUM spect  
 PROBHD 5 mm QNP 1H/13  
 PULPROG zg30  
 TD 32768  
 SOLVENT CDC13  
 NS 16  
 DS 0  
 SWH 10964.912 Hz  
 FIDRES 0.334623 Hz  
 AQ 1.4942708 sec  
 RG 512  
 DW 45.600 usec  
 DE 6.00 usec  
 TE 297.2 K  
 D1 1.00000000 sec  
 TD0 1

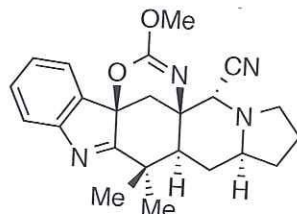
===== CHANNEL f1 =====  
 NUC1 1H  
 P1 14.00 usec  
 PL1 -1.00 dB  
 SFO1 500.1340010 MHz

F2 - Processing parameters  
 SI 32768  
 SF 500.1300138 MHz  
 WDW EM  
 SSB 0  
 LB 0.30 Hz  
 GB 0  
 PC 1.00

7.58  
7.56  
7.44  
7.44  
7.42  
7.41  
7.40  
7.39  
7.27  
7.26  
7.24

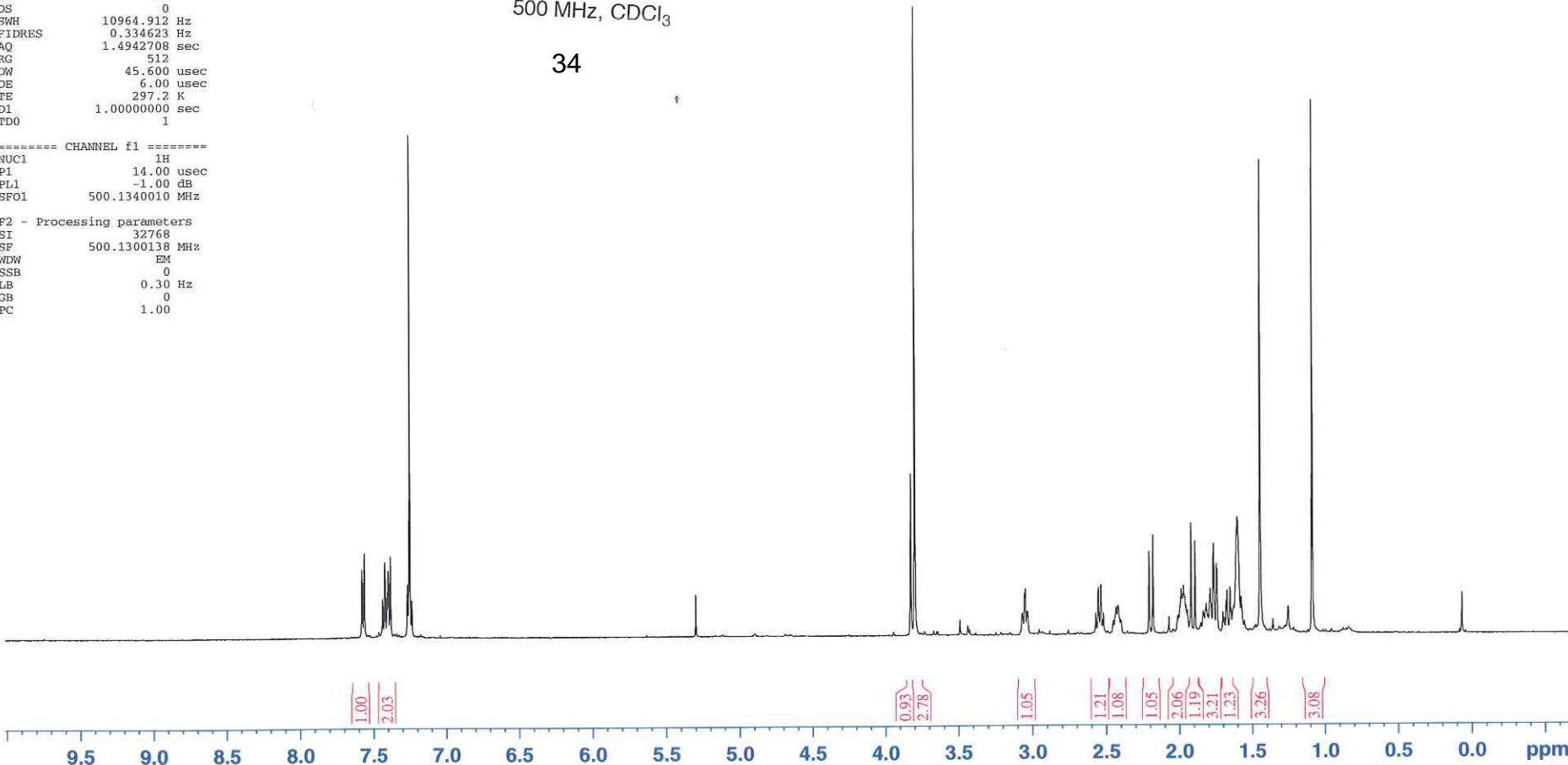
Proton24

3.83  
3.80  
3.07  
3.07  
3.05  
3.05  
3.04  
3.03  
2.57  
2.55  
2.53  
2.52  
2.43  
2.42  
2.18  
1.99  
1.97  
1.92  
1.89  
1.81  
1.76  
1.74  
1.74  
1.67  
1.45  
1.09



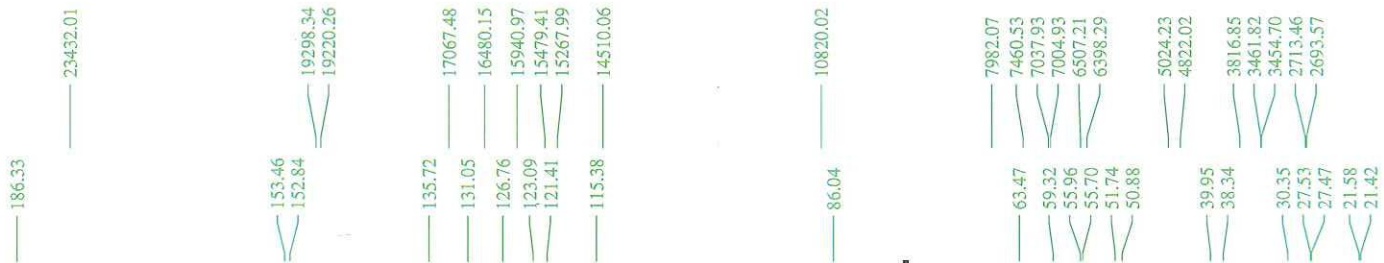
500 MHz, CDCl<sub>3</sub>

34



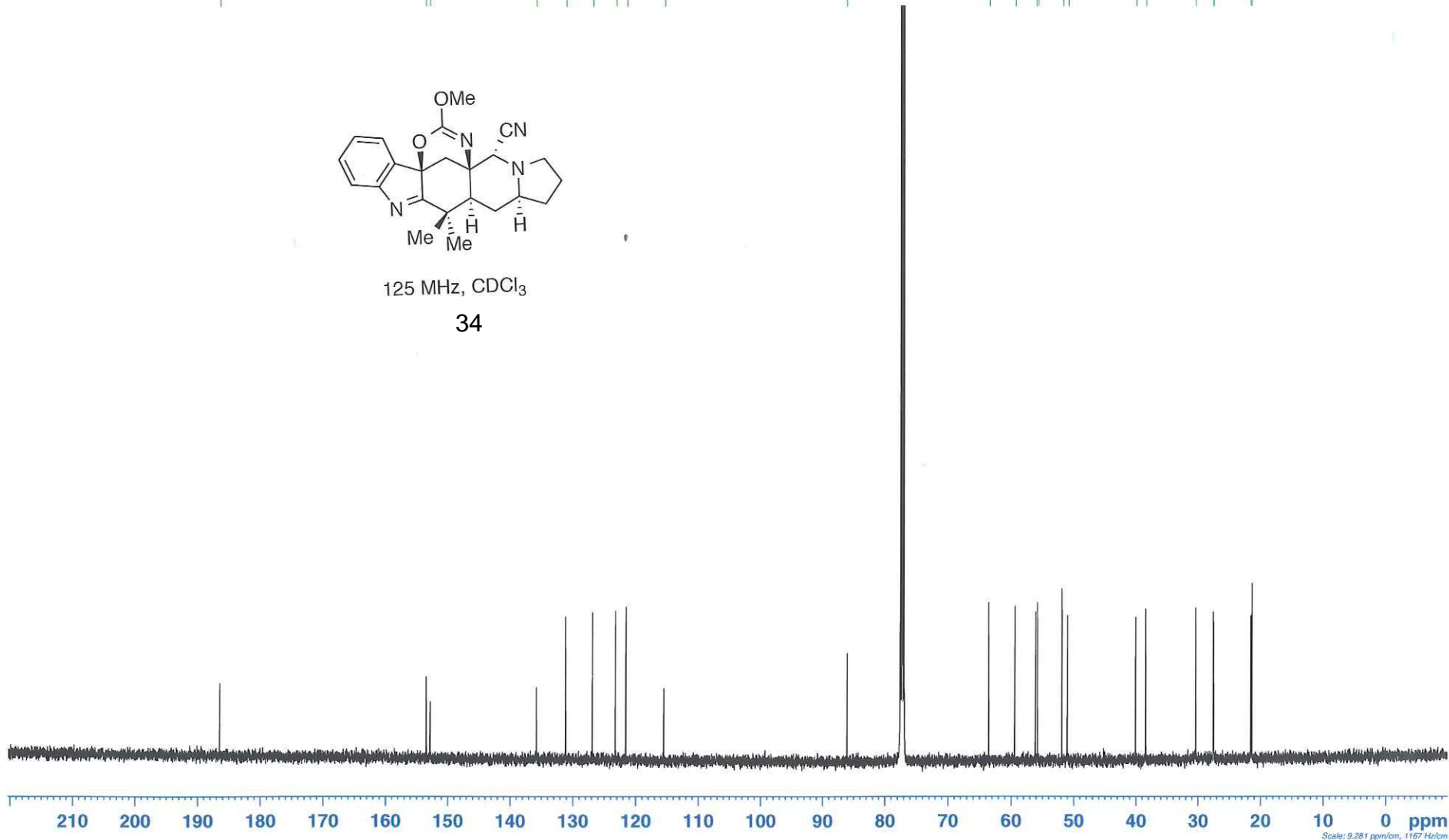
AL-3-122-C13

Carbon



125 MHz, CDCl<sub>3</sub>

34



Scale: 9.281 ppm/cm, 1167 Hz/cm



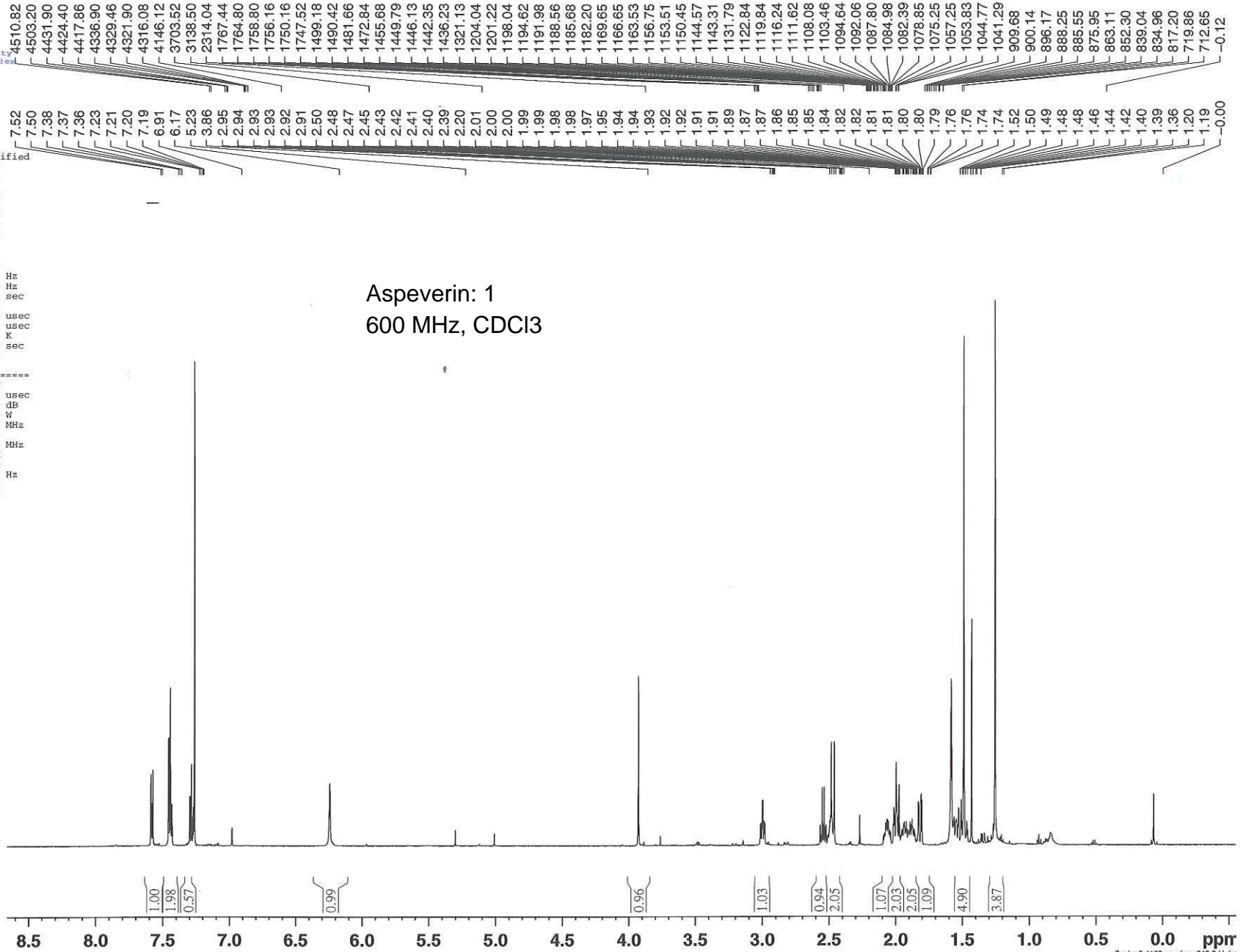


NMR Analytical Core Facility  
Coker/eller Research Laboratories  
430 E 67th St  
New York, NY 10021

group Danishefsky  
\* levinsoa al-3-147-repurified (10 1) CDCI3 24.0C July 24, 2014\_11:16:33 Bruker AVIII 600MHz RRL1326: janggeum zg30 : 1H 7.500 ppm \*  
\_ProtonBC CDCI3 /opt/users/levinsoa levinsoa 18

NAME al-3-147-repurified  
EXPNO 10  
PROCNO 1  
Date\_ 20140724  
Time 11.18  
INSTRUM spect  
PROBHD 5 mm PATXO 19F  
PULPROG zg30  
TD 65536  
SOLVENT CDCI3  
NS 24  
DS 0  
SWH 13227.514 Hz  
FIDRES 0.201836 Hz  
AQ 2.4773109 sec  
RG 322  
DW 37.800 usec  
DE 9.29 usec  
TE 297.2 K  
D1 1.00000000 sec  
TDO 1

===== CHANNEL f1 =====  
NUC1 1H  
P1 12.90 usec  
PL1 -1.30 dB  
PL1W 27.78522110 W  
SFO1 600.1345010 MHz  
SI 65536  
SF 600.1300173 MHz  
WDW EM  
SSB 0  
LB 0.31 Hz  
GB 0  
PC 1.00

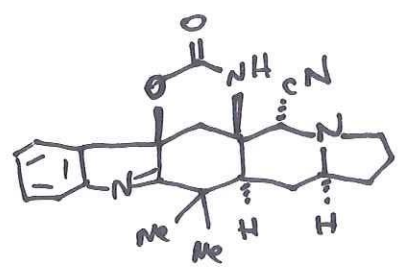


Scale: 0.4162 ppm/cm, 249.8 Hz/cm

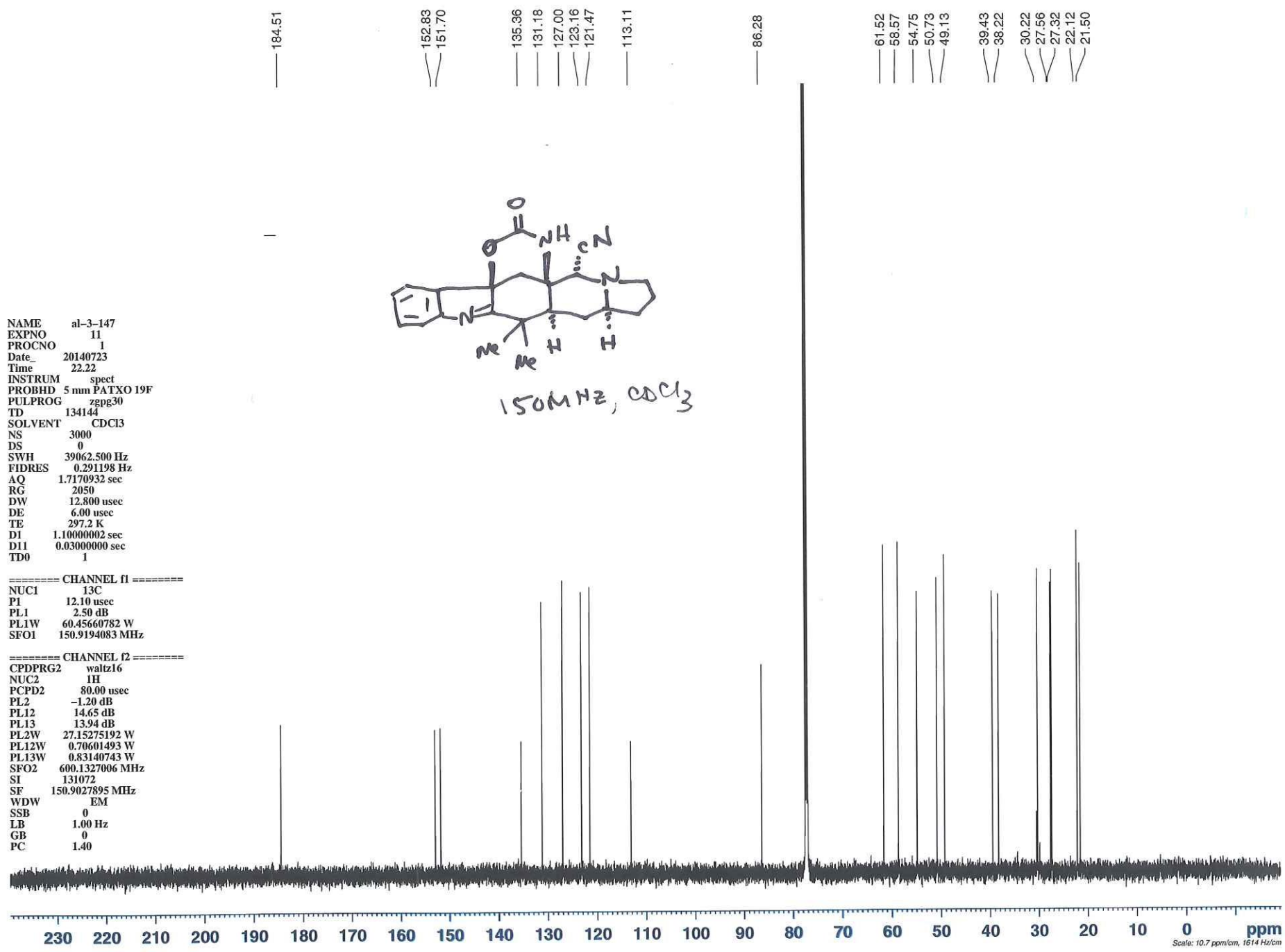
NAME al-3-147  
 EXPNO 11  
 PROCNO 1  
 Date\_ 20140723  
 Time 22.22  
 INSTRUM spect  
 PROBHD 5 mm PATXO 19F  
 PULPROG zgpg30  
 TD 134144  
 SOLVENT CDCl3  
 NS 3000  
 DS 0  
 SWH 39062.500 Hz  
 FIDRES 0.291198 Hz  
 AQ 1.7170932 sec  
 RG 2050  
 DW 12.800 usec  
 DE 6.00 usec  
 TE 297.2 K  
 DI 1.10000002 sec  
 D11 0.03000000 sec  
 TD0 1

===== CHANNEL f1 =====  
 NUC1 13C  
 P1 12.10 usec  
 PL1 2.50 dB  
 PL1W 60.45660782 W  
 SFO1 150.9194083 MHz

===== CHANNEL f2 =====  
 CPDPRG2 waltz16  
 NUC2 1H  
 PCPD2 80.00 usec  
 PL2 -1.20 dB  
 PL12 14.65 dB  
 PL13 13.94 dB  
 PL2W 27.15275192 W  
 PL12W 0.70601493 W  
 PL13W 0.83140743 W  
 SFO2 600.1327006 MHz  
 SI 131072  
 SF 150.9027895 MHz  
 WDW EM  
 SSB 0  
 LB 1.00 Hz  
 GB 0  
 PC 1.40



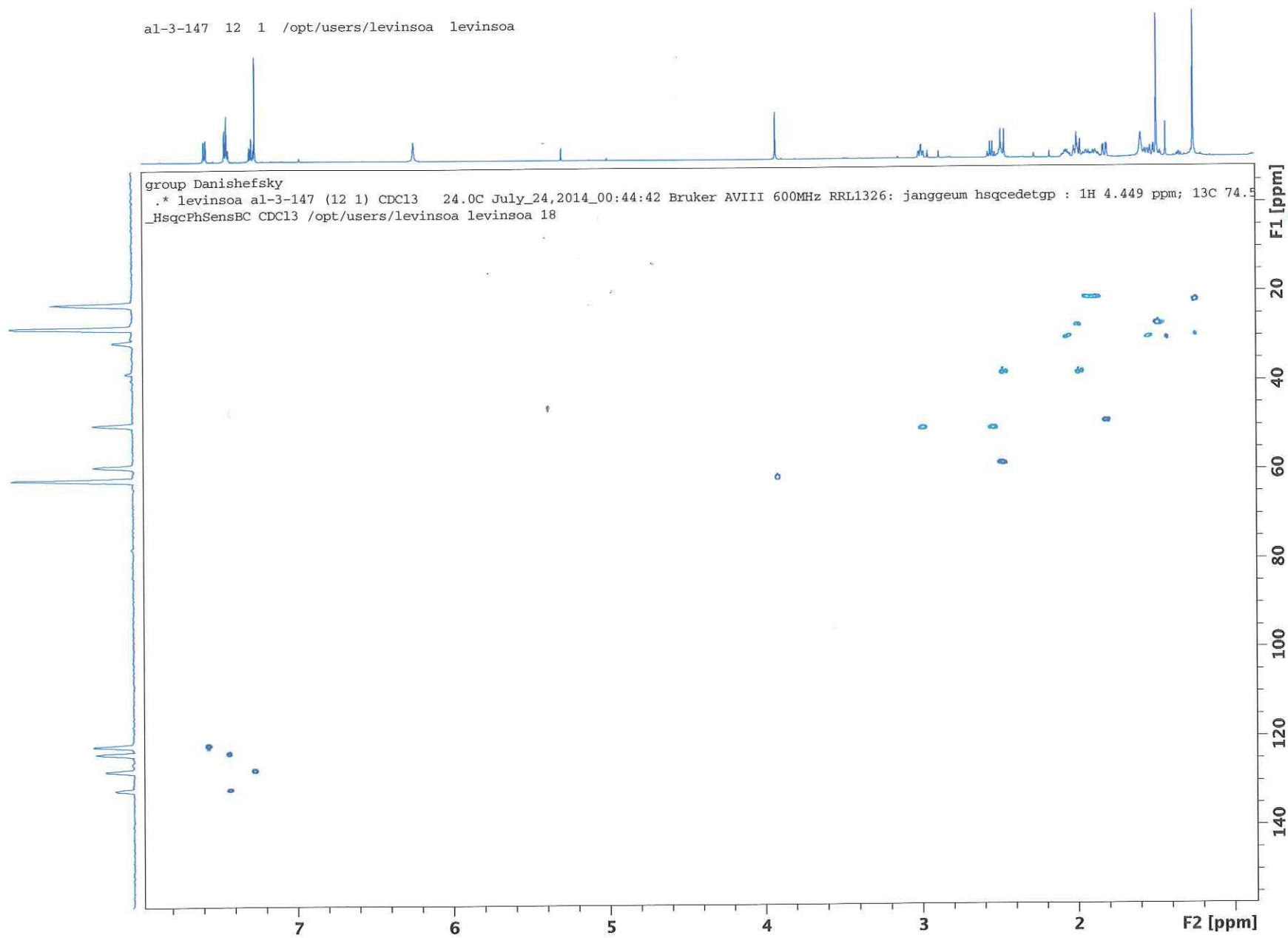
150 MHz, CDCl<sub>3</sub>



Scale: 10.7 ppm/cm, 1614 Hz/cm

Aspeverin (1) : HSQC spectrum

al-3-147 12 1 /opt/users/levinsoa levinsoa

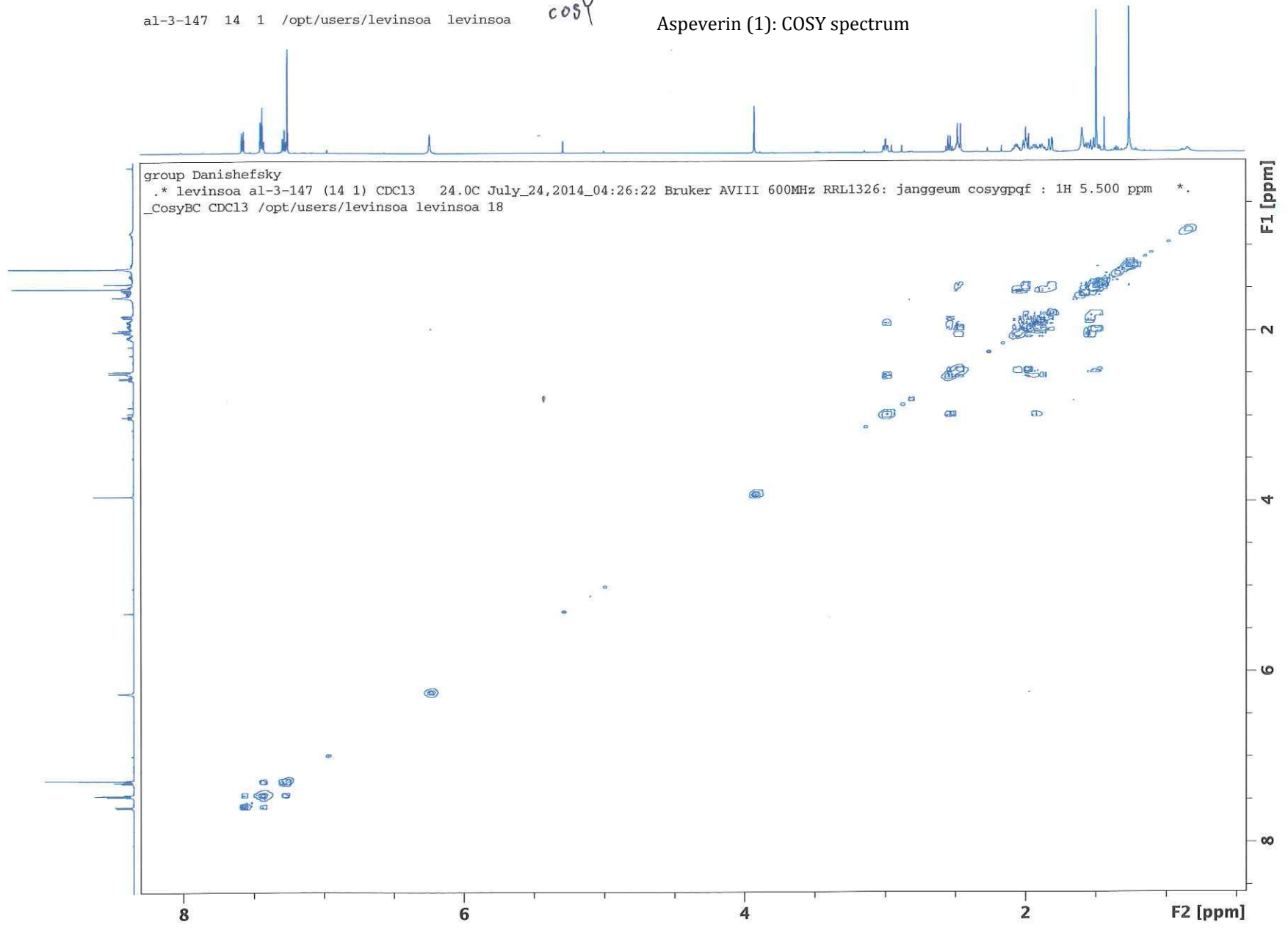


~~HSQC~~ HSQC

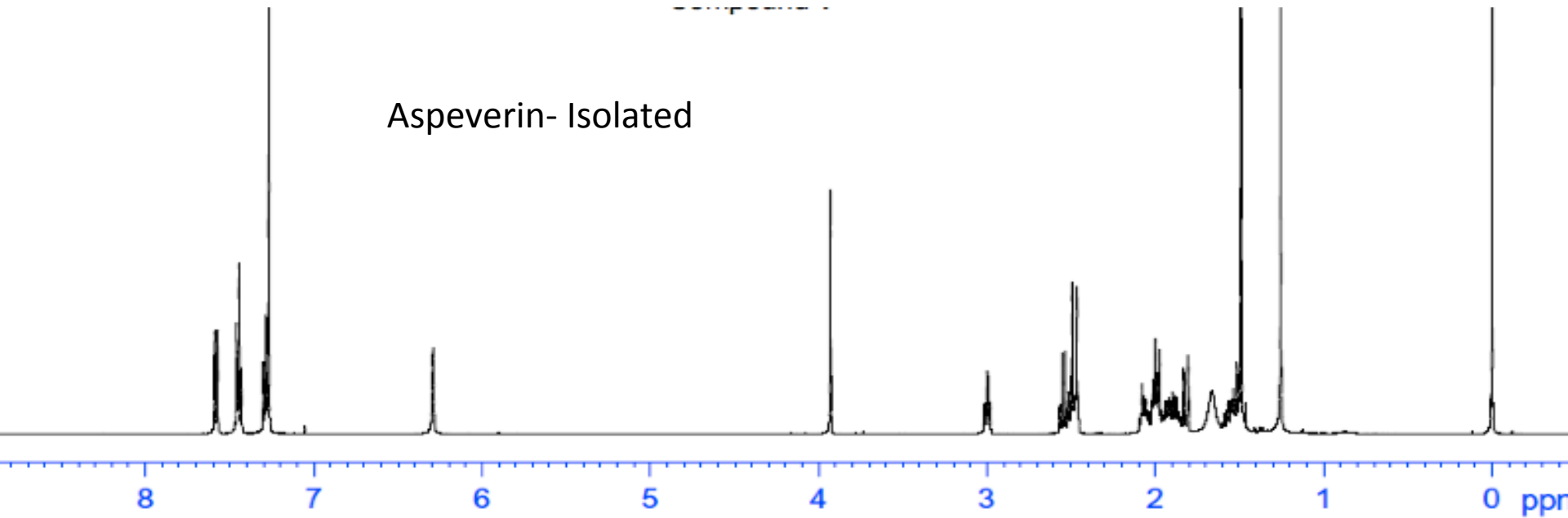
al-3-147 14 1 /opt/users/levinsoa levinsoa

*cosy*

### Aspeverin (1): COSY spectrum

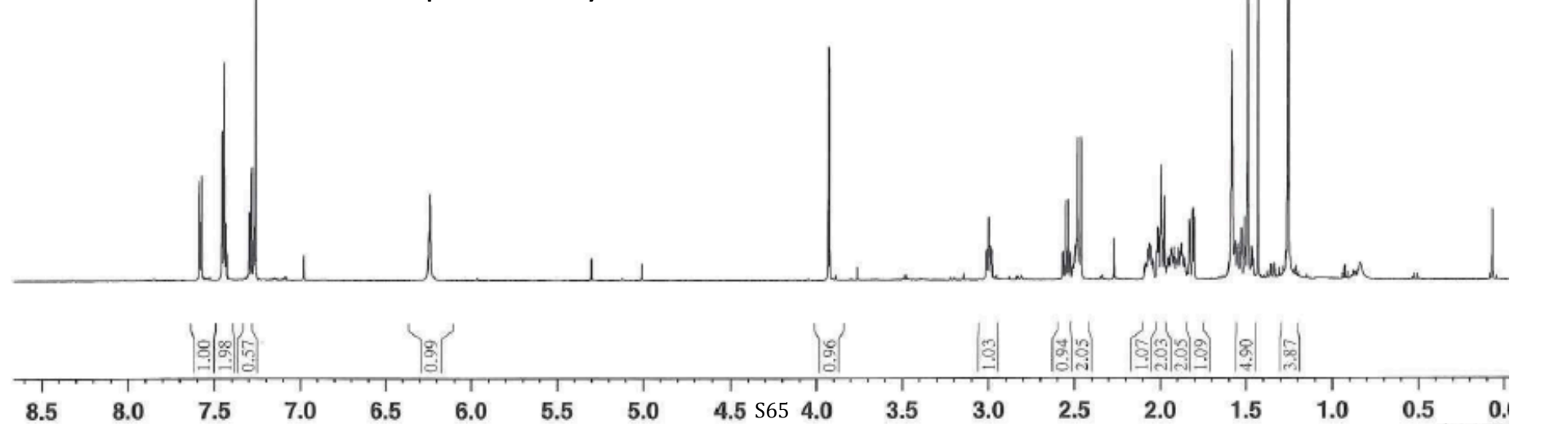


Aspeverin- Isolated

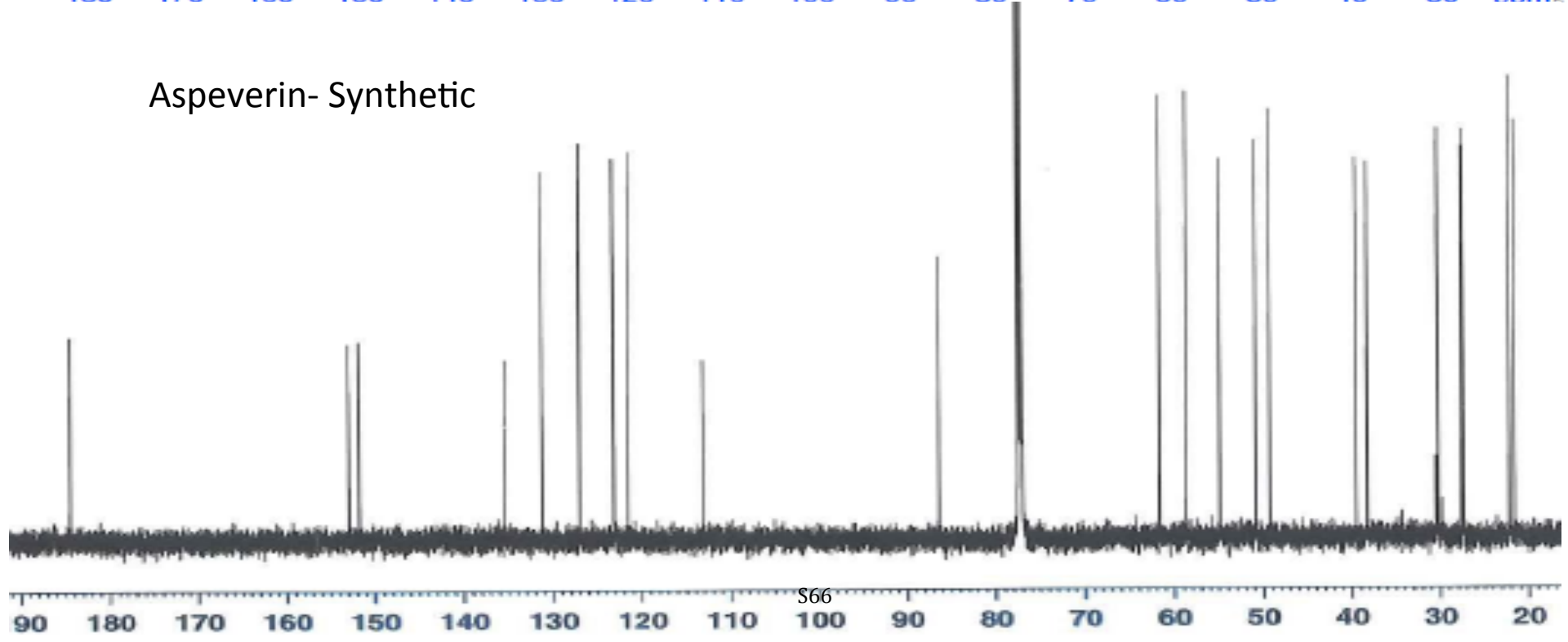
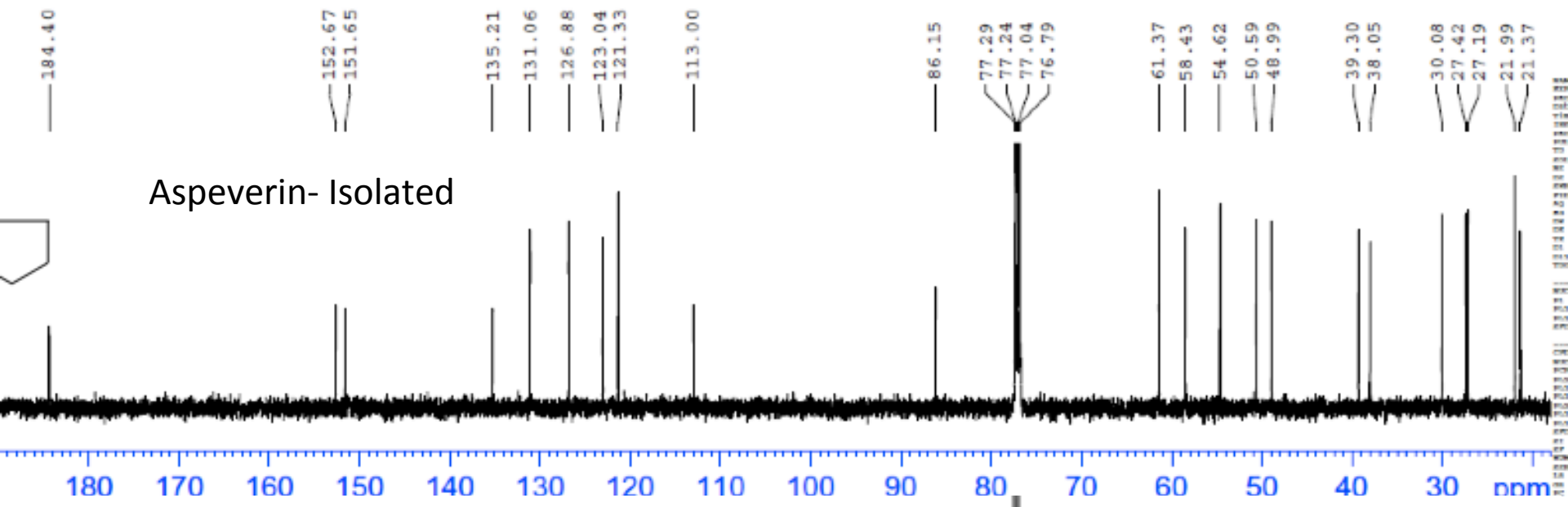


1.01  
2.07  
0.94  
1.00  
0.98  
1.00  
1.17  
1.88  
1.20  
2.11  
2.10  
1.10  
2.01  
1.87  
3.47  
3.40

Aspeverin- Synthetic

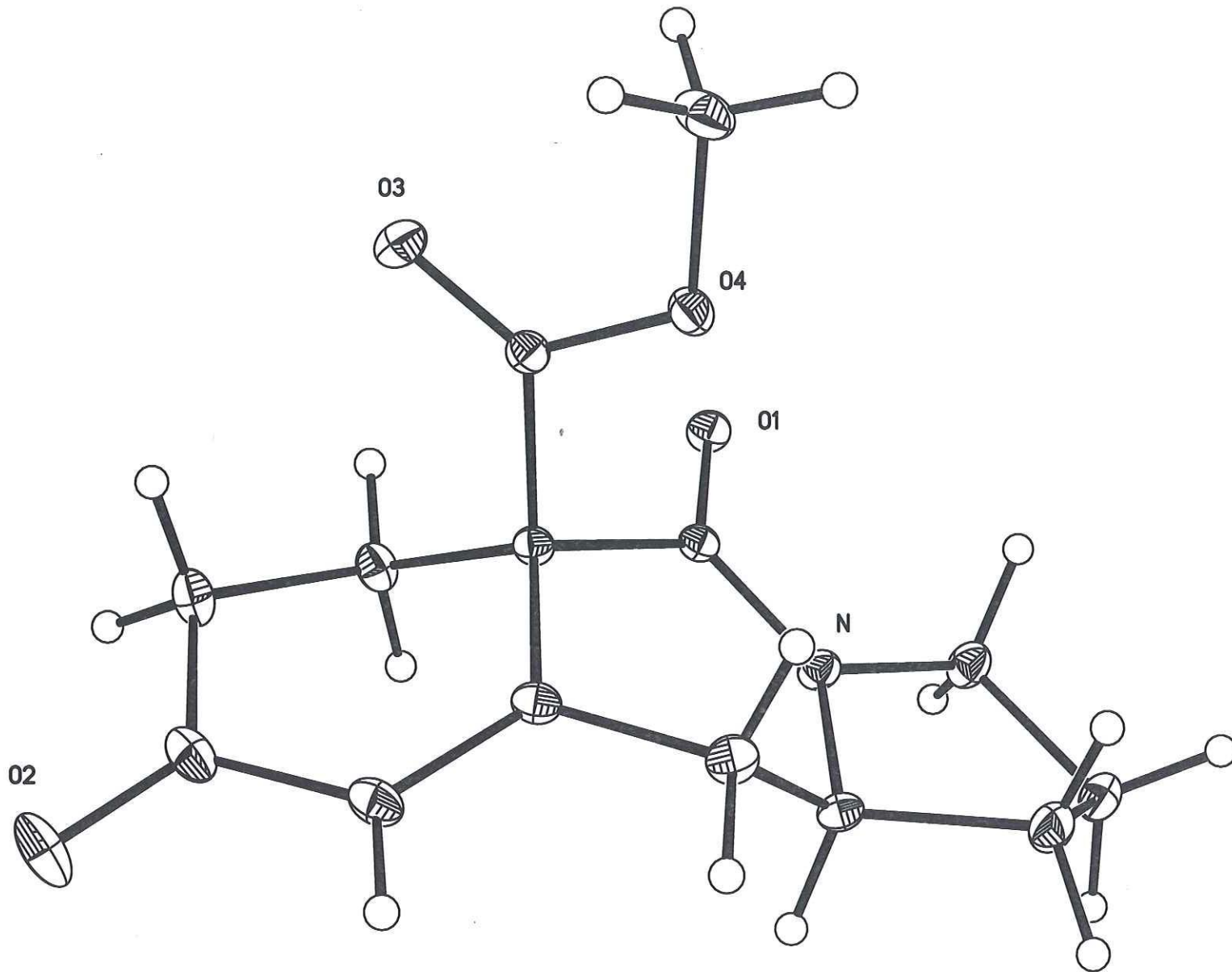


1.00  
1.98  
0.57  
0.99  
0.96  
1.03  
0.94  
2.05  
1.07  
2.03  
2.05  
1.09  
4.90  
3.87



20

ORTEP drawing, compound 20





## Compound 20

Table 1. Crystal data and structure refinement for adams10.

Identification code	adams10
Empirical formula	C14 H17 N O4
Formula weight	263.28
Temperature	130(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P -1
Unit cell dimensions	a = 6.9183(8) Å    alpha = 68.2765(13) deg.
	b = 9.7324(11) Å    beta = 79.1821(15) deg.
	c = 10.5986(12) Å    gamma = 79.3466(15) deg.
Volume	645.93(13) Å <sup>3</sup>
Z, Calculated density	2, 1.354 Mg/m <sup>3</sup>
Absorption coefficient	0.099 mm <sup>-1</sup>
F(000)	280
Crystal size	0.77 x 0.56 x 0.44 mm
Theta range for data collection	2.086 to 30.489 deg.
Limiting indices	-9<=h<=9, -13<=k<=13, -15<=l<=15
Reflections collected / unique	10400 / 3912 [R(int) = 0.0282]
Completeness to theta = 25.242	99.9 %
Absorption correction	Empirical
Max. and min. transmission	0.7461 and 0.6568
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	3912 / 0 / 173
Goodness-of-fit on F <sup>2</sup>	1.017
Final R indices [I>2sigma(I)]	R1 = 0.0375, wR2 = 0.1070
R indices (all data)	R1 = 0.0398, wR2 = 0.1104
Extinction coefficient	n/a
Largest diff. peak and hole	0.490 and -0.274 e.Å <sup>-3</sup>