# Protecting-Group-Free Total Synthesis of (–)-Lycopodine via Phosphoric Acid-Promoted Alkyne Aza-Prins Cyclization

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**Electronic Supplementary Information**

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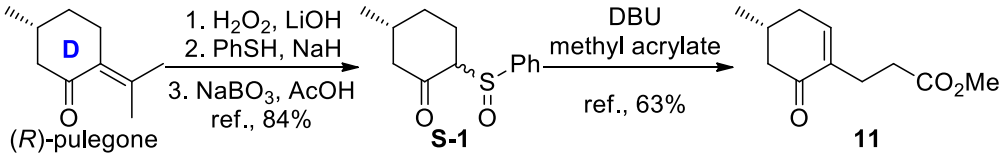
## General Information

All oxygen- and moisture-sensitive reactions were carried out under an argon atmosphere. All solvents were purified and dried by standard methods prior to use. All commercially available reagents were used without further purification unless otherwise noted. Column chromatography was performed on silica gel (200–300 mesh) unless otherwise mentioned.

Melting points were measured on a melting point apparatus and are uncorrected. Optical rotations were measured using a 0.1-mL cell with a 1-cm path length on Rudolph Autopol IV automatic polarimeter, and concentrations (c) were reported in g/100 mL. $^{1}$H NMR and $^{13}$C NMR spectra were recorded on Bruker AM-400 MHz instrument. Chemical shifts are denoted in ppm ($\delta$), and calibrated by using residual undeuterated solvent ($CDCl_3$, $\delta$ 7.27 for $^{1}$H NMR and 77.0 for $^{13}$C NMR; tetramethylsilane, $\delta$ 0.00 for $^{1}$H NMR and 0.00 for $^{13}$C NMR) as internal reference. Infrared (IR) spectra were recorded on a Nicolet Nexus 670 FT-IR spectrometer. High-resolution mass spectral analysis (HRMS) data were measured on a Bruker APEXII mass spectrometer by means of the electrospray ionization (ESI) technique. The X-ray single-crystal determination was performed on a Bruker APEX II X-ray single crystal diffractometer.

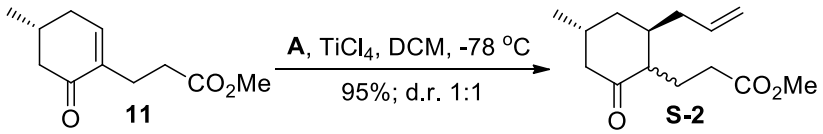
# Experimental Procedures

### *1. (R)-Methyl 3-(4-methyl-6-oxocyclohex-1-enyl)propanoate 11*

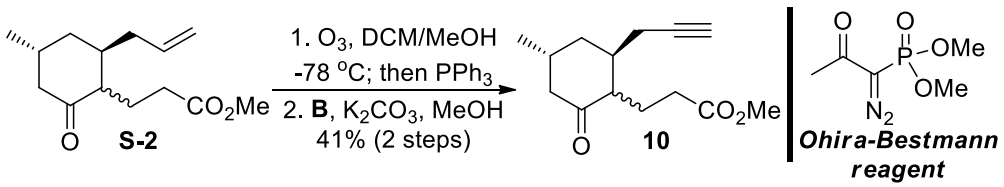



(*R*)-Methyl 3-(4-methyl-6-oxocyclohex-1-enyl)propanoate **(11)**[1]. Data for **11**: a light yellow oil; $[\alpha]_D^{25.3}$ = –57 °(*c* = 1.0, $CHCl_3$) { lit.[5] $[\alpha]_D^{20}$ = –39 °(*c* = 0.63, $CHCl_3$)}; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 6.69–6.72 (m, 1H), 3.60 (s, 3H), 2.32–2.48 (m, 6H), 1.95–2.19 (m, 3H), 1.00 (d, *J* = 6.4 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 199.2, 173.4, 145.5, 137.6, 51.4, 46.4, 34.2, 32.9, 30.4, 25.2, 21.0.

### *2. Methyl 3-((4R,6S)-4-methyl-2-oxo-6-(prop-2-yn-1-yl)cyclohexyl)propanoate 10 (Mehod A)*




**Methyl 3-((2*R*,4*R*)-2-allyl-4-methyl-6-oxocyclohexyl)propanoate (S-2)**. $TiCl_4$ (3.2 mL, 28.347 mmol, 2 equiv.) was added dropwise to a cooled (–78 ℃) solution of enone **11** (2.778 g, 14.173 mmol) and allyltrimethylsilane (**A**) (6.7 mL, 42.520 mmol, 3 equiv.) in DCM (90 mL) under an argon atmosphere. The reaction was stirred for 20 min at –78 ℃ and then saturated $NaHCO_3$ (aq.) was added. The resulting slurry was allowed to gradually warm (2 h) to room temperature and extracted with DCM (4 × 50 mL). The combined organic layers were dried over anhydrous $Na_2SO_4$, filtered and concentrated under reduced pressure. Flash chromatography of the residue (hexanes/EtOAc, 15:1) provided alkene-ketone **S-2** (3.220 g, 95%, d.r. 1:1) as a pale yellow oil. Data for **S-2**: $[\alpha]_D^{24.1}$ = +13 °(*c* = 1.0, $CHCl_3$); IR (neat) $\nu_{max}$ = 3077, 2954, 2925, 2873, 2851, 1738, 1709, 1640, 1438, 1274, 1250, 1213, 1197, 1170, 997, 915 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 5.75 – 5.58 (m, 1H), 5.04 – 4.93 (m, 2H), 3.63 (s, 3H), 2.55 – 1.58 (m, 12H), 1.54 – 1.38 (m, 1H), 0.92 – 0.97 (dd, *J* = 10.5, 6.3 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 213.4, 211.6, 173.8, 173.5, 136.2, 135.7, 117.0, 116.4, 53.6, 52.7, 51.5, 51.4, 50.2, 47.1, 40.4, 39.1, 37.9, 36.5, 34.2, 31.9, 31.70, 31.66, 29.5, 29.3, 24.6, 22.2, 21.8, 21.0; HRMS (ESIMS) calcd for $C_{14}H_{23}O_3$: $[M+H]^+$ 239.1642; found: 239.1644.

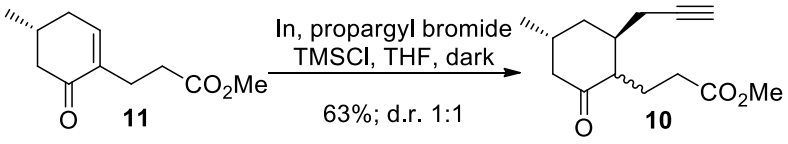



**Methyl 3-((4*R*,6*S*)-4-methyl-2-oxo-6-(prop-2-yn-1-yl)cyclohexyl)propanoate (10)**. Through a stirred solution of alkene-ketone **S-2** (3.077 g, 12.928 mmol) in DCM/MeOH (5:1, 65 mL) at –78 ℃ was bubbled ozone gas (0.5 h). After the color of the mixture changed to blue, argon gas was bubbled to this resulting solution for 10 min, followed by the addition of triphenylphosphine (7.452 g, 28.442 mmol, 2.2 equiv.) at –78 ℃. The reaction was allowed to gradually warm (1 h) to room temperature and kept at that temperature for 4 h. And then the resulting solution was concentrated

under reduced pressure. Flash chromatography of the residue (hexanes/EtOAc, 5:1→3:2) provided corresponding aldehyde (2.960 g, 95%) as a colorless oil which was used immediately for the next reaction due to the instability of the aldehyde.

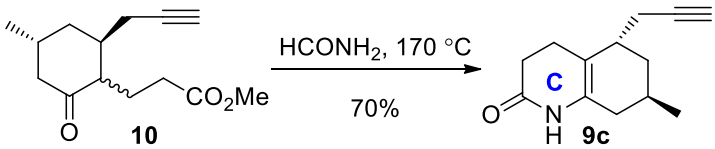
$K_2CO_3$ (3.404 g, 24.666 mmol, 2 equiv.) was added to a stirred solution of the above aldehyde (2.960 g, 12.333 mmol) in anhydrous MeOH (120 mL) under an Ar atmosphere at room termperature. **Ohira-Bestmann reagent** dimethyl (1-diazo-2-oxopropyl)-phosphonate (**B**) (2.842 g, 14.800 mmol, 1.2 equiv.) was dissolved in anhydrous MeOH (7 ml) and added to the reaction mixture. After stirred for 1.5 h, the reaction was quenched with saturated $NaHCO_3$ (aq.), MeOH was removed under reduced pressure and aqueous phase was extracted with $Et_2O$ (4 × 50 mL). The combined organic layers were washed with brine (50 mL), dried over anhydrous $Na_2SO_4$, filtered and concentrated under reduced pressure. Flash chromatography of the residue (hexanes/EtOAc, 20:1→5:1) provided alkyne-ketone **10** (1.260 g, 43%) as a colorless oil. Data for **10**: $[\alpha]_D^{24.0}$ = –16 ° (*c* = 1.0, $CHCl_3$); IR (neat) $\nu_{max}$ = 3282, 2955, 2927, 2872, 2854, 2371, 1737, 1709, 1455, 1437, 1252, 1200, 1215, 1170, 646 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 3.65 (s, 3H), 2.60 – 1.65 (m, 13H), 1.57 – 1.45 (m, 1H), 0.94 – 1.04 (dd, *J* = 26.1, 6.5 Hz, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ = 212.3, 211.0, 173.62, 173.55, 81.9, 81.3, 70.6, 70.0, 52.9, 52.0, 51.5, 50.1, 47.3, 40.0, 38.0, 37.0, 34.8, 31.7, 31.6, 29.6, 29.4, 23.4, 23.1, 22.1, 21.6, 20.3, 17.6; HRMS (ESIMS) calcd for $C_{14}H_{21}O_3$: $[M+H]^+$ 237.1485; found: 237.1487.

### *Methyl 3-((4R,6S)-4-methyl-2-oxo-6-(prop-2-yn-1-yl)cyclohexyl)propanoate 10 (Mehod B)*




**Methyl 3-((4*R*,6*S*)-4-methyl-2-oxo-6-(prop-2-yn-1-yl)cyclohexyl)propanoate (10)**. To a solution of indium [indium powder (99.99%), 1.907 g, 16.582 mmol, 5 equiv.] in THF (9 mL) was added propargyl bromide (80 wt.% solution in toluene, 3.700 g, 24.872 mmol, 7.5 equiv.) under a nitrogen atmosphere at room temperature. After stirred for 45 min, chlorotrimethylsilane (5.26 mL, 41.454 mmol, 12.5 mmol) and a solution of enone **11** (650 mg, 3.316 mmol) in THF (1 mL) was successively added to reaction mixture. After 32 h in dark room, the reaction mixture was poured into pH 7.0 buffer solution (35 mL, $Na_2HPO_4/NaH_2PO_4$) which was pre-cooled at 0 ℃ and the aqueous layer was extracted with ether (4 × 80 mL). The combined organic layers were washed with water (60 mL), brine (60 mL), dried with anhydrous $Na_2SO_4$, filtered and concentrated under reduced pressure. Flash chromatography of the residue (hexanes/EtOAc, 20:1→5:1) provided alkyne-ketone **10** (493 mg, 63%) as a colorless oil.

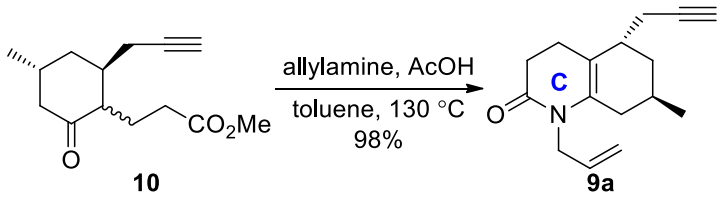
### *3. (5S,7R)-7-Methyl-5-(prop-2-yn-1-yl)-3,4,5,6,7,8-hexahydroquinolin-2(1H)-one 9c*




**(5*S*,7*R*)-7-Methyl-5-(prop-2-yn-1-yl)-3,4,5,6,7,8-hexahydroquinolin-2(1H)-one (9c)**. A mixture of alkyne-ketone **10** (229 mg, 0.970 mmol) in formamide (3.9 mL) was heated at 170 ℃ for 3h. After cooling, water was added to the mixture and the resulting suspension was extracted with EtOAc (4 × 20 mL). The combined organic layers were washed with brine (20 mL), dried over anhydrous $Na_2SO_4$, filtered and concentrated under reduced pressure. Flash chromatography of the residue (hexanes/EtOAc, 2:1) provided alkyne-enamide **9c** (138 mg, 70%) as a white solid. Data for **9c**: m.p. 117–118 ℃; $[\alpha]_D^{24.5}$ = +26 ° (*c* = 1.0, $CHCl_3$); IR (neat) $\nu_{max}$ = 3276, 3231, 3164, 3096, 2952, 2927, 2885,

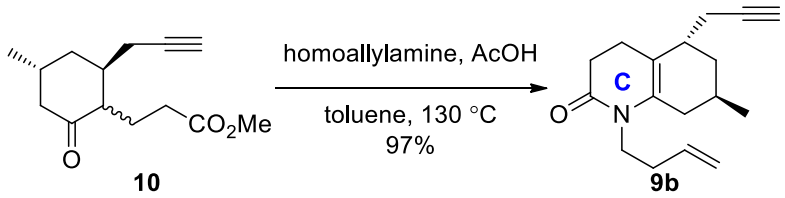
2868, 2372, 1736, 1701, 1673, 1457, 1389, 1376, 1237, 1200, 1047, 803, 757, 661, 518 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 8.25 (br d, 1H), 2.51 – 2.28 (m, 5H), 2.15 – 1.95 (m, 4H), 1.86 (d, *J* = 12.8 Hz, 2H), 1.71 (dd, *J* = 15.8, 10.3 Hz, 1H), 1.34 (td, *J* = 12.8, 5.3 Hz, 1H), 0.97 (d, *J* = 6.3 Hz, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ = 171.9, 129.8, 111.0, 83.4, 69.3, 36.9, 34.9, 34.6, 30.8, 24.0, 23.8, 22.7, 21.3; HRMS (ESIMS) calcd for $C_{13}H_{18}NO$: $[M+H]^+$ 204.1383; found: 204.1386.

### *4. (5S,7R)-1-allyl-7-methyl-5-(prop-2-yn-1-yl)-3,4,5,6,7,8-hexahydroquinolin-2(1H)-one 9a*




**(5*S*,7*R*)-1-allyl-7-methyl-5-(prop-2-yn-1-yl)-3,4,5,6,7,8-hexahydroquinolin-2(1H)-one (9a)**. To a stirred solution of alkyne-ketone **10** (246 mg, 1.042 mmol) in toluene (8 mL) was added glacial AcOH (0.8 mL) and allylamine (390 $\mu$L, 5.210 mmol, 5 equiv.) successively, and then the reaction was heated to 130 ℃ for 3 h. After cooling to room temperature, saturated $NaHCO_3$ (aq.) was added to adjust the pH to 8 and the resulting suspension was extracted with EtOAc (4 × 20 mL). The combined organic layers were washed with brine (20 mL), dried over anhydrous $Na_2SO_4$, filtered and concentrated under reduced pressure. Flash chromatography of the residue (hexanes/EtOAc, 5:1→3:1) provided alkyne-enamide **9a** (247 mg, 98%) as a colorless oil. Data for **9a**: $[\alpha]_D^{24.6}$ = –12 °(*c* = 1.0, $CHCl_3$); IR (neat) $\nu_{max}$ = 3299, 3264, 2951, 2927, 2870, 2371, 1671, 1637, 1391, 1279, 1189, 1135, 919, 715, 631 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 5.83 – 5.73 (m, 1H), 5.09 – 5.00 (m, 2H), 4.24 (dd, *J* = 4.5, 1.8 Hz, 2H), 2.54 – 2.08 (m, 8H), 1.98 (t, *J* = 2.4 Hz, 1H), 1.94 – 1.83 (m, 2H), 1.76 – 1.66 (m, 1H), 1.32 (td, *J* = 13.0, 5.9 Hz, 1H), 1.00 (d, *J* = 6.5 Hz, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ = 170.0, 134.1, 132.7, 116.0, 114.9, 83.3, 69.4, 42.5, 37.5, 34.1, 33.5, 31.8, 24.3, 23.8, 23.0, 21.4; HRMS (ESIMS) calcd for $C_{16}H_{22}NO$: $[M+H]^+$ 244.1696; found: 244.1700.

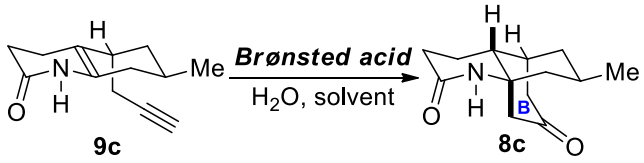
### *5. (5S,7R)-1-(but-3-en-1-yl)-7-methyl-5-(prop-2-yn-1-yl)-3,4,5,6,7,8-hexahydroquinolin-2(1H)-one 9b*




**(5*S*,7*R*)-1-(but-3-en-1-yl)-7-methyl-5-(prop-2-yn-1-yl)-3,4,5,6,7,8-hexahydroquinolin-2(1H)-one (9b)**. To a stirred solution of alkyne-ketone **10** (236 mg, 1.000 mmol) in toluene (8 mL) was added glacial AcOH (0.8 mL) and homoallylamine (3-buten-1-amine) (470 $\mu$L, 5.000 mmol, 5 equiv.) successively, and then the reaction was heated to 130 ℃ for 3 h. After cooling to room temperature, saturated $NaHCO_3$ (aq.) was added to adjust the pH to 8 and the resulting suspension was extracted with EtOAc (4 × 20 mL). The combined organic layers were washed with brine (20 mL), dried over anhydrous $Na_2SO_4$, filtered and concentrated under reduced pressure. Flash chromatography of the residue (hexanes/EtOAc, 10:1→3:1) provided alkyne-enamide **9b** (249 mg, 97%) as a white solid. Data for **9b**: m.p. 59–60 ℃; $[\alpha]_D^{24.7}$ = –28 °(*c* = 1.0, $CHCl_3$); IR (neat) $\nu_{max}$ = 3303, 3243, 2953, 2925, 2870, 2840, 2363, 1665, 1394, 1227, 1190, 1135, 993, 916, 719, 635 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 5.75 (ddt, *J* = 17.1, 10.2, 7.0 Hz, 1H), 5.05 – 4.98 (m, 2H), 3.70 – 3.57 (m, 2H), 2.47 – 2.32 (m, 4H), 2.27 – 2.13 (m, 5H), 2.08 – 2.00 (m, 1H), 1.98 – 1.82 (m, 3H), 1.77 –

1.70 (m, 1H), 1.34 (td, $J$ = 12.9, 5.8 Hz, 1H), 1.02 (d, $J$ = 6.5 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 170.2, 135.0, 132.3, 116.9, 116.6, 83.2, 69.4, 39.7, 37.5, 34.2, 33.9, 33.6, 32.0, 24.4, 23.6, 22.9, 21.4; HRMS (ESIMS) calcd for $C_{17}H_{24}NO$: $[M+H]^+$ 258.1852; found: 258.1855.

### *6. Tabel 1. Brønsted acid inducing aza-Prins cyclization of enamide and synthesis of Tricyclic lactam-ketone 8c*



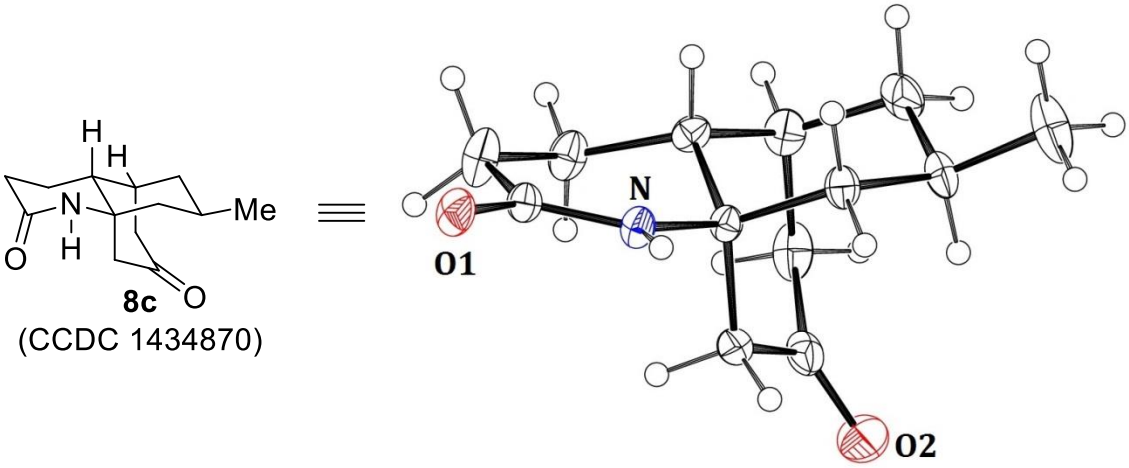

| entry[a] | solvent (volume ratio) | t/h | **9c**[b] | **8c**[b] |
|---|---|---|---|---|
| 1 | THF/6 M HCl (aq.), 1:1 | 12 | 8% | 23% |
| 2 | THF/6 M $H_2SO_4$ (aq.) , 1:1 | 12 | 8% | 46% |
| 3 | THF/HCOOH/$H_2O$, 2:1:1 | 22 | 75% | / |
| 4 | THF/TFA/$H_2O$, 2:1:1 | 22 | 67% | / |
| 5 | THF/85% $H_3PO_4$ (aq.), 1:1 | 36 | 8% | 84% |
| 6 | HCOOH/$H_2O$, 1:1 | 66 | 55% | / |
| **7**[c] | **HCOOH/85% $H_3PO_4$ (aq.), 1:1** | **21** | **/** | **96%** |

[a] Reaction conditions: alkyne-enamide **9c** (12 mg, 0.0591 mmol) in solvent (1 mL), rt, air. [b] Isolated yields. [c] alkyne-enamide **9c** (70 mg, 0.345 mmol) in solvent (4 mL). TFA = trifluoroacetic acid.

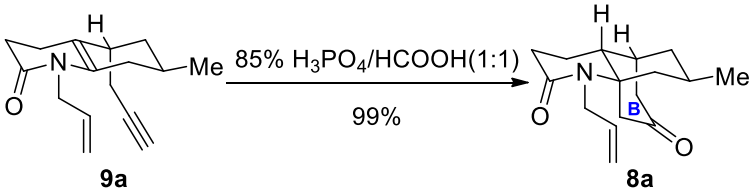
**Tricyclic lactam-ketone 8c**. In an ordinary 10 mL round- bottomed flask vial equipped with a magnetic stirring bar, to alkyne-enamide **9c** (12 mg, 0.0591 mmol or 70 mg, 0.345 mmol) and solvent (1 or 4 mL) indicated in Tables 1 was added and the reaction mixture was stirred at room temperature for the time indicated in Tables 1. At 0 ℃, 6 N NaOH (aq.) (5 or 20 mL) was added dropwise to adjust the pH to 8 and then the resulting slurry was extracted with $CHCl_3$ (4 × 10 mL). The combined organic layers were dried over anhydrous $Na_2SO_4$, filtered and concentrated under reduced pressure. Flash chromatography of the residue provided unreacted alkyne-enamide **9c** (hexanes/EtOAc, 1:1) as a white solid and tricyclic lactam-ketone **8c** (EtOAc/MeOH, 10:0→10:1) as a white solid. Data for **8c**: m.p. ~260 ℃ (decomposed); $[\alpha]_D^{24.8}$ = –6 ° ($c$ = 1.0, $CHCl_3$); IR (neat) $\nu_{max}$ = 3169, 3072, 3027, 2955, 2918, 2872, 1738, 1701, 1664, 1638, 1626, 1392, 1375, 1307, 1243, 1162, 1115, 1046, 793, 756, 609 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 6.78 (br s, 1H), 2.61 – 2.44 (m, 5H), 2.33 (br s, 1H), 2.26 (d, $J$ = 17.2 Hz, 1H), 2.06 – 1.94 (m, 1H), 1.85 – 1.72 (m, 4H), 1.65 – 1.51 (m, 1H), 1.39 – 1.25 (m, 2H), 0.89 (d, $J$ = 6.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 208.7, 171.1, 55.7, 51.5, 49.1, 41.8, 41.4, 41.0, 34.4, 31.4, 25.0, 22.4, 21.9; HRMS (ESIMS) calcd for $C_{13}H_{20}NO_2$: $[M+H]^+$ 222.1489; found: 222.1492.

### *Configuration assignment of tricyclic lactam-ketone 8c*

The configuration of tricyclic lactam-ketone **8c** (CCDC 1434870) was confirmed by X-ray crystallographic analysis.



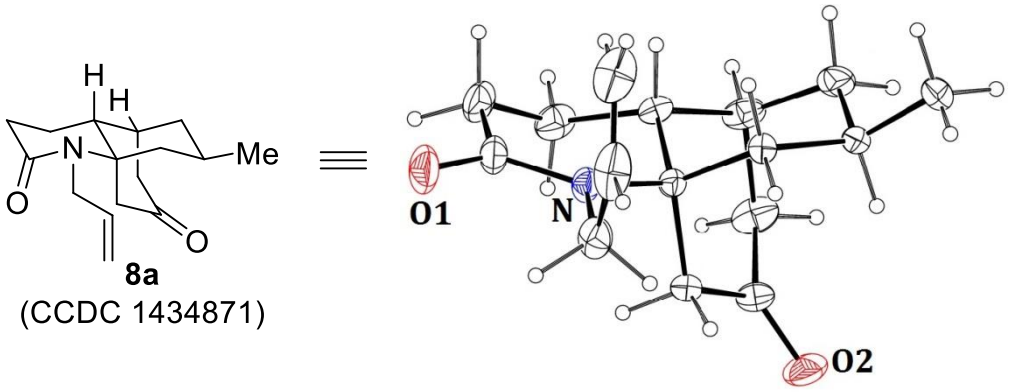

### *7. Tricyclic lactam-ketone 8a*



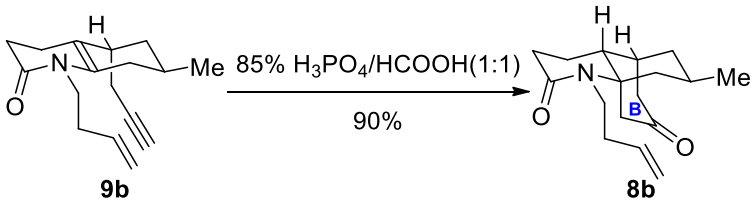

**Tricyclic lactam-ketone 8a**. In an ordinary round-bottomed flask vial equipped with a magnetic stirring bar, to alkyne-enamide **9a** (247 mg, 1.016 mmol) and HCOOH/85% $H_3PO_4$ (1:1, 3 mL) was added and the reaction mixture was stirred at room temperature for 19 h. At 0 ℃, 15 mL 6 N NaOH (aq.) was added dropwise to adjust the pH to 8 and then the resulting slurry was extracted with EtOAc (4 × 30 mL). The combined organic layers were dried over anhydrous $Na_2SO_4$, filtered and concentrated under reduced pressure. Flash chromatography of the residue (EtOAc/MeOH, 50:0→50:1) provided tricyclic lactam-ketone **8a** (263 mg, 99%) as a white solid. Data for **8a**: m.p. 126–127 ℃; $[\alpha]_D^{24.9}$ = –41 °(*c* = 1.0, $CHCl_3$); IR (neat) $\nu_{max}$ = 3454, 2951, 2923, 2871, 1735, 1705, 1636, 1440, 1401, 1340, 1246, 1223, 1116, 956, 946, 921, 753 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 5.81 (ddd, *J* = 22.8, 10.7, 5.6 Hz, 1H), 5.14 – 5.06 (m, 2H), 4.20 (dd, *J* = 15.8, 5.4 Hz, 1H), 3.66 (dd, *J* = 15.8, 5.7 Hz, 1H), 2.77 (d, *J* = 17.1 Hz, 1H), 2.65 – 2.40 (m, 4H), 2.33 (br d, *J* = 1.7 Hz, 1H), 2.26 (d, *J* = 17.2 Hz, 1H), 2.12 (dd, *J* = 13.1, 3.9 Hz, 1H), 2.04 – 1.92 (m, 1H), 1.89 (d, *J* = 13.6 Hz, 1H), 1.77 – 1.69 (m, 2H), 1.59 – 1.45 (m, 1H), 1.30 (td, *J* = 12.8, 3.8 Hz, 1H), 1.20 (td, *J* = 12.6, 1.6 Hz, 1H), 0.90 (d, *J* = 6.2 Hz, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ = 208.6, 169.2, 135.2, 116.0, 60.9, 48.9, 47.3, 43.5, 42.3, 41.7, 41.0, 35.2, 32.5, 25.4, 22.6, 22.2; HRMS (ESIMS) calcd for $C_{16}H_{24}NO_2$: $[M+H]^+$ 262.1802; found: 262.1804.

### *Absolute configuration assignment of tricyclic lactam-ketone 8a*

The absolute configuration of tricyclic lactam-ketone **8a** (CCDC 1434871) was confirmed by X-ray crystallographic analysis, and the intensity data were collected on an Agilent SuperNova (Dual, Cu at zero, Eos) diffractometer using graphite-monochromated Cu Kα radiation.

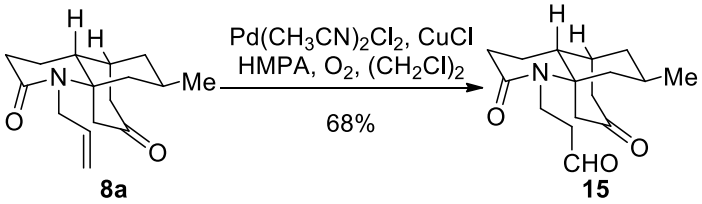



### *8. Tricyclic lactam-ketone 8b*



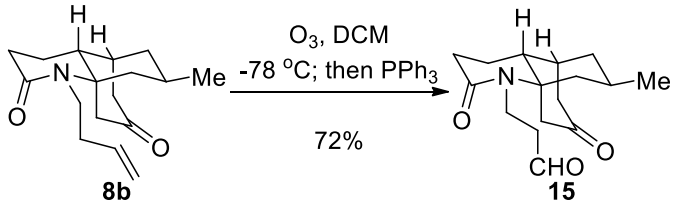

**Tricyclic lactam-ketone 8b**. In an ordinary round-bottomed flask vial equipped with a magnetic stirring bar, to alkyne-enamide **9b** (249 mg, 0.969 mmol) and HCOOH/85% $H_3PO_4$ (1:1, 3 mL) was added and the reaction mixture was stirred at room temperature for 18 h. At 0 ℃, 15 mL 6 N NaOH (aq.) was added dropwise to adjust the pH to 8 and then the resulting slurry was extracted with EtOAc (4 × 30 mL). The combined organic layers were dried over anhydrous $Na_2SO_4$, filtered and concentrated under reduced pressure. Flash chromatography of the residue (EtOAc) provided tricyclic lactam-ketone **8b** (241 mg, 90%) as a white solid which was very difficult to crystallize. Data for **8b**: m.p. 93–95 ℃; $[\alpha]_D^{25.0}$ = –40 ° (*c* = 1.0, $CHCl_3$); IR (neat) $\nu_{max}$ = 3460, 2951, 2926, 2871, 1736, 1707, 1636, 1452, 1405, 1364, 1340, 1246, 1223, 1116, 914, 899, 754 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 5.76 (ddt, *J* = 17.1, 10.2, 6.8 Hz, 1H), 5.06 – 4.97 (m, 2H), 3.58 (ddd, *J* = 13.5, 10.9, 5.3 Hz, 1H), 2.88 (ddd, *J* = 13.6, 10.9, 5.0 Hz, 1H), 2.73 (d, *J* = 17.0 Hz, 1H), 2.60 – 2.36 (m, 5H), 2.31 (br t, *J* = 2.0 Hz, 1H), 2.24 (d, *J* = 17.2 Hz, 1H), 2.15 – 2.05 (m, 2H), 2.01 – 1.88 (m, 1H), 1.85 (d, *J* = 13.6 Hz, 1H), 1.73 – 1.68 (m, 2H), 1.60 – 1.46 (m, 1H), 1.30 (td, *J* = 12.8, 3.9 Hz, 1H), 1.21 (td, *J* = 12.4, 1.6 Hz, 1H), 0.91 (d, *J* = 6.2 Hz, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ = 208.6, 169.3, 135.3, 116.2, 60.6, 48.6, 47.3, 42.3, 41.7, 41.00, 40.98, 35.2, 33.9, 32.7, 25.4, 22.6, 22.2; HRMS (ESIMS) calcd for $C_{17}H_{26}NO_2$: $[M+H]^+$ 276.1958; found: 276.1961.

### *9. Keto aldehyde 15 (Mehod A)*



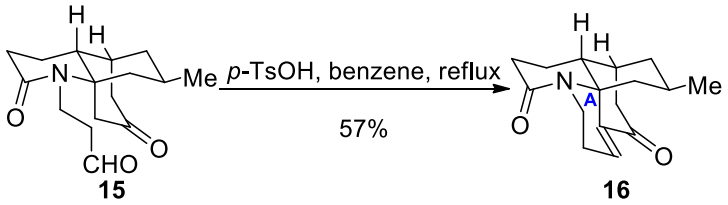

**Keto aldehyde 15**. To a solution of tricyclic lactam-ketone **8a** (105 mg, 0.4 mmol) in dry 1,2-dichloroethane (1.2 mL) was added $PdCl_2(MeCN)_2$ (11 mg, 0.04 mmol, 0.1 equiv.), CuCl (4 mg, 0.04 mmol, 0.1 equiv.) and HMPA (140 $\mu$L, 0.8 mmol, 2 equiv.). After the reaction mixture was stirred under oxygen atmosphere (balloon pressure) at room temperature for 43 h, 1,2-dichloroethane was removed under reduced pressure and water was added to the mixture. The resulting suspension was extracted with EtOAc (4 × 20 mL). The combined organic layers were washed with brine (2 ×20 mL), dried over anhydrous $Na_2SO_4$, filtered and concentrated under reduced pressure. Flash chromatography of the residue (EtOAc) provided keto aldehyde **15** (76 mg, 68%) as a colorless oil.

### *Keto aldehyde 15 (Mehod B)*



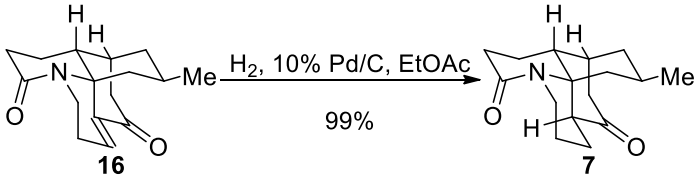

**Keto aldehyde 15**. Through a stirred solution of tricyclic lactam-ketone **8b** (329 mg, 1.196 mmol) in DCM (10 mL) at –78 ℃ was bubbled ozone gas (15 min). After the color of the mixture changed to light blue, argon gas was bubbled to this resulting solution for 10 min, followed by the addition of triphenylphosphine (690 mg, 2.632 mmol, 2.2 equiv.) at –78 ℃. The reaction was allowed to gradually warm (1 h) to room temperature and kept at that temperature for 12 h. And then the resulting solution was concentrated under reduced pressure. Flash chromatography of the residue (EtOAc) provided keto aldehyde **15** (239 mg, 72%) as a colorless oil. Data for **15**: $[\alpha]_D^{28.4}$ = –50 °(*c* = 1.0, $CHCl_3$); IR (neat) $\nu_{max}$ = 3419, 2951, 2925, 2731, 1708, 1626, 1456, 1409, 1366, 1341, 1307, 1223, 1161, 1118, 754 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 9.75 (s, 1H), 3.85 (ddd, *J* = 14.5, 8.1, 6.7 Hz, 1H), 3.23 (ddd, *J* = 13.9, 8.5, 5.1 Hz, 1H), 2.90 – 2.81 (m, 1H), 2.74 (d, *J* = 17.0 Hz, 1H), 2.61 – 2.39 (m, 5H), 2.34 (br d, *J* = 1.8 Hz, 1H), 2.27 (d, *J* = 17.2 Hz, 1H), 2.11 (dd, *J* = 12.4, 3.6 Hz, 1H), 2.01 – 1.89 (m, 1H), 1.87 (d, *J* = 13.5 Hz, 1H), 1.75 – 1.70 (m, 2H), 1.57 – 1.50 (m, 1H), 1.31 (td, *J* = 12.9, 4.0 Hz, 1H), 1.21 – 1.14 (m, 1H), 0.91 (d, *J* = 6.2 Hz, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ = 208.1, 200.3, 169.8, 61.0, 48.4, 47.1, 44.4, 42.3, 41.6, 41.0, 35.23, 35.18, 32.6, 25.4, 22.5, 22.2; HRMS (ESIMS) calcd for $C_{16}H_{24}NO_3$: $[M+H]^+$ 278.1751; found: 278.1748.

## *10. Tetracyclic enone 16*




**Tetracyclic enone 16**. A solution of keto aldehyde **15** (228 mg, 0.823 mmol) and *p*-TSA (78 mg, 0.412 mmol, 0.5 equiv.) in benzene (60 mL) was heated at reflux with removal of water through a Dean-Stark apparatus under an argon atmosphere for 30 h. After cooling the mixture to room termperature, the resulting solution was concentrated under reduced pressure. Flash chromatography of the residue (hexanes/EtOAc, 1:2→0:2) provided tetracyclic enone **16** (122 mg, 57%) as a colorless oil. Data for **16**: $[\alpha]_D^{28.4}$ = +113 °(*c* = 1.0, $CHCl_3$); IR (neat) $\nu_{max}$ = 3452, 3274, 2952, 2922, 2872, 1686, 1641, 1615, 1457, 1401, 1376, 1350, 1269, 1241, 1222, 1199, 1125, 754 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 6.90 (t, *J* = 3.7 Hz, 1H), 4.65 (dd, *J* = 13.8, 7.7 Hz, 1H), 3.17 (ddd, *J* = 13.7, 11.5, 5.4 Hz, 1H), 2.62 – 2.42 (m, 4H), 2.40 – 2.29 (m, 3H), 2.17 (dt, *J* = 20.4, 5.0 Hz, 1H), 1.94 (d, *J* = 11.5 Hz, 1H), 1.76 (d, *J* = 12.9 Hz, 1H), 1.70 – 1.61 (m, 2H), 1.57 – 1.45 (m, 1H), 1.40 (td, *J* = 12.8, 4.1 Hz, 1H), 1.27 (t, *J* = 12.0 Hz, 1H), 0.93 (d, *J* = 6.1 Hz, 3H).; $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ = 196.9, 170.1, 140.2, 137.9, 60.2, 48.9, 42.9, 41.4, 40.9, 34.0, 33.8, 33.5, 25.8, 25.4, 23.5, 22.1; HRMS (ESIMS) calcd for $C_{16}H_{22}NO_2$: $[M+H]^+$ 260.1645; found: 260.1648.

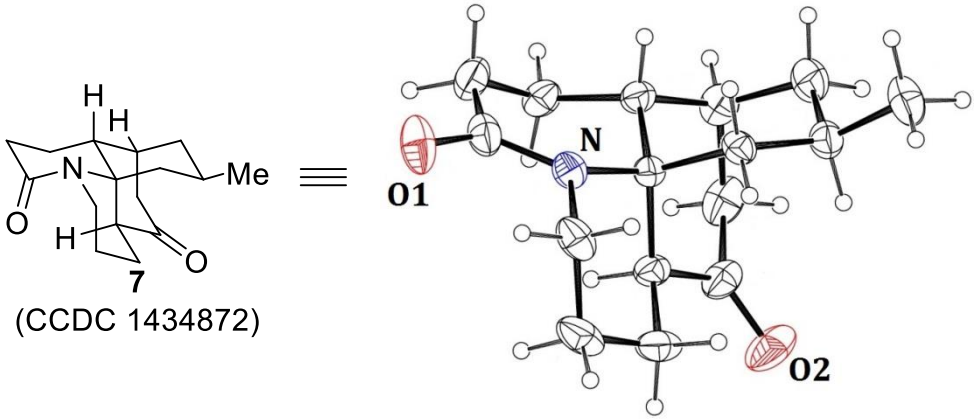
## *11. Lycopodine lactam 7 (tetracyclic ketolactam 7)*



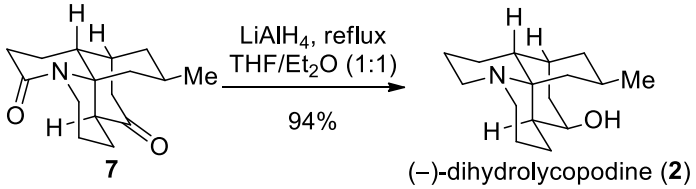

**Lycopodine lactam 7**. To a solution of tetracyclic enone **16** (83 mg, 0.320 mmol) in EtOAc (10 mL) was added 10% Pd/C (73 mg). The mixture was stirred at room temperature under hydrogen atmosphere (balloon pressure) at room temperature for 6 h, and then filtered over a pad of silica gel, followed by washing with EtOAc (3 × 30 mL). The combined filtrate was concentrated under reduced pressure to provide lycopodine lactam **7** (83 mg, 99%) as a white solid. Data for **7**: m.p. 157–159 ℃; $[\alpha]_D^{28.5}$ = –15 °(*c* = 1.0, $CHCl_3$); IR (neat) $\nu_{max}$ = 3399, 3254, 2952, 2871, 1706, 1636, 1457, 1435, 1407, 1379, 1349, 1311, 1267, 1258, 1225, 1187, 1142, 1117, 754, 665 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 4.59 (dd, *J* = 13.8, 5.3 Hz, 1H), 2.91 (td, *J* = 13.4, 3.2 Hz, 1H), 2.68 – 2.47 (m, 5H), 2.36 – 2.33 (m, 1H), 2.30 (d, *J* = 16.1 Hz, 1H), 2.24 – 2.11 (m, 2H), 1.95 (d, *J* = 13.3 Hz, 1H), 1.79 – 1.69 (m, 3H), 1.68 – 1.63 (m, 1H), 1.57 – 1.42 (m, 2H), 1.37 (td, *J* = 13.2, 4.0 Hz, 1H), 0.99 (t, *J* = 12.8 Hz, 1H), 0.91 (d, *J* = 6.2 Hz, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ = 209.2, 168.6, 61.6, 52.8, 43.6, 42.4, 41.7, 36.4, 35.9, 33.3, 25.2, 24.9, 22.5, 22.0, 19.1; HRMS (ESIMS) calcd for $C_{16}H_{24}NO_2$: $[M+H]^+$ 262.1802; found: 262.1799.

### *Absolute configuration assignment of lycopodine lactam 7*

The absolute configuration of lycopodine lactam **7** (CCDC 1434872) was confirmed by X-ray crystallographic analysis, and the intensity data were collected on an Agilent SuperNova (Dual, Cu at zero, Eos) diffractometer using graphite-monochromated Cu Kα radiation.

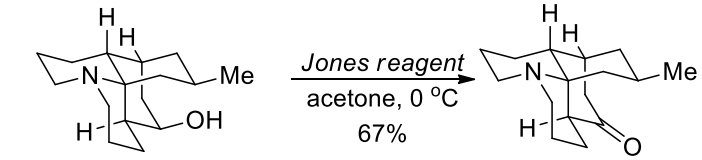



### *12. Lycopodine (1) and Dihydrolycopodine (2)*

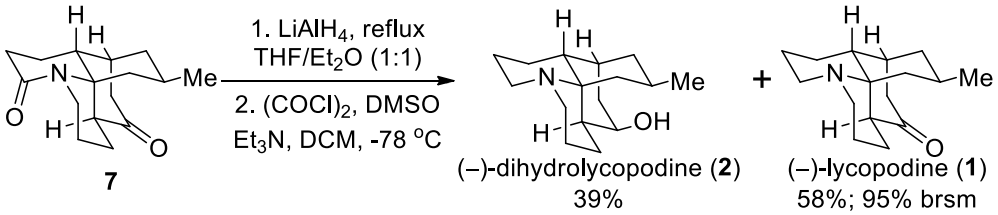



To a suspension of $LiAlH_4$ (45 mg, 1.150 mmol, 15 equiv.) in dry $Et_2O$ (2 mL) at room temperature under an argon atmosphere was added dropwise a solution of lycopodine lactam **7** (20 mg, 0.0766 mmol) in THF (2 mL), and the resulting mixture was heated at 60 ℃ for 6 h. After cooling to 0 ℃, excess hydride was quenched by adding dropwise water (50 $\mu$L), 10% NaOH (aq., 100 $\mu$L) and warter (150 $\mu$L) successively. The resulting slurry was filtered over a pad of Celite, followed by washing with $Et_2O$ (6 × 10 mL). The combined filtrate were dried with anhydrous $Na_2SO_4$, filtered and concentrated under reduced pressure. Flash chromatography of the residue (DCM/MeOH, 50:1→10:1) over basic alumina (100–200 mesh) provided (–)-dihydrolycopodine (**2**)[2] (18 mg, 94%) as a white solid.

Data for (–)-dihydrolycopodine (**2**): m.p. 164–166 ℃ (lit.[2b] m.p. = 166–169 ℃; lit.[2c] m.p. = 168–169 ℃); $[\alpha]_D^{25.5}$ = –39 °(*c* = 1.0, $CHCl_3$), $[\alpha]_D^{25.5}$ = –32.1 °(*c* = 0.56, EtOH){ lit.[2b] $[\alpha]_D^{25}$ = –33 °(*c* = 0.56, EtOH); lit.[2c] $[\alpha]_D$ = –38 °(*c* = 0.18, EtOH)}; IR (neat) $\nu_{max}$ = 3405, 2924, 2863, 1454, 1304, 1239, 1215, 1190, 1114, 1097, 1061, 990, 941, 754, 658 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 3.95 (t, *J* = 5.7 Hz, 1H), 3.45 (td, *J* = 13.9, 3.7 Hz, 1H), 3.16 (td, *J* = 12.1, 3.4 Hz, 1H), 2.92 – 2.77 (m, 1H), 2.61 (dd, *J* = 13.2, 5.8 Hz, 1H), 2.56 – 2.48 (m, 2H), 2.33 (ddd, *J* = 12.5, 5.6, 3.0 Hz, 1H), 2.11 – 2.03 (m, 1H), 2.03 – 1.92 (m, 1H), 1.83 (ddd, *J* = 25.9, 12.8, 4.3 Hz, 1H), 1.76 – 1.58 (m, 4H), 1.55 – 1.43 (m, 4H), 1.39 – 1.33 (m, 2H), 1.29 – 1.23 (m, 1H), 1.19 (dd, *J* = 12.3, 4.9 Hz, 1H), 0.87 (d, *J* = 6.4 Hz, 3H), 0.79 (t, *J* = 12.8 Hz, 1H); $^{13}C$ NMR (100 MHz, $CDCl_3$) [2a]: $\delta$ = 68.4, 55.3, 47.2, 47.0, 45.6, 42.9, 41.8, 35.4, 33.7, 32.5, 26.4, 24.7, 24.0, 23.4, 23.3, 20.5; HRMS (ESIMS) calcd for $C_{16}H_{28}NO$: $[M+H]^+$ 250.2165; found: 250.2161.




**Jones Oxidation**. To a solution of dihydrolycopodine (**2**) (30 mg, 0.120 mmol) in acetone (5 mL) was added dropwise Jones reagent (2.7 *M*, 190 $\mu$L) at 0 ℃. The resulting solution was stirred at 0 ℃ for 10 min and then was quenched with addition of isopropyl alcohol (1.5 mL). The resulting mixture was filtered over a pad of Celite, followed by washing with DCM (6 × 10 mL). The combined filtrate was dried over anhydrous $Na_2SO_4$, filtered and concentrated under reduced pressure. Flash chromatography of the residue over basic alumina (100–200 mesh) (DCM/MeOH, 10:0→10:1) provided (–)-lycopodine (**1**) (20 mg, 67%) as a white solid. ***lycopodine is very sensitive to silica gel.***



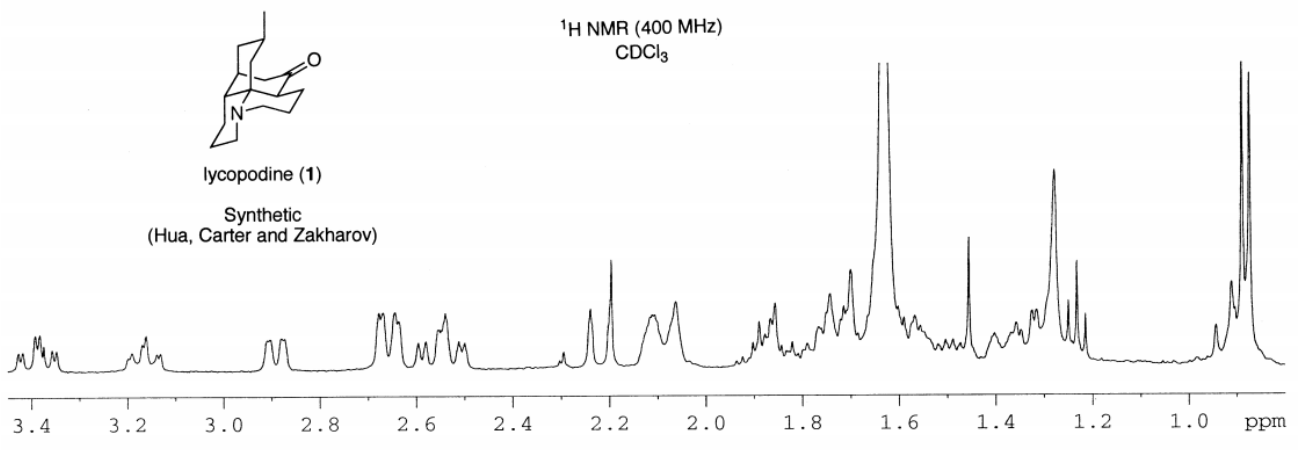

**Swern Oxidation**. To a suspension of $LiAlH_4$ (90 mg, 2.299 mmol, 15 equiv.) in dry $Et_2O$ (3 mL) at room temperature under an argon atmosphere was added dropwise a solution of lycopodine lactam **7** (40 mg, 0.153 mmol) in THF (3 mL), and the resulting mixture was heated at 60 ℃ for 6 h. After cooling to 0 ℃, excess hydride was quenched by adding dropwise water (90 $\mu$L), 10% NaOH (aq., 180 $\mu$L) and warter (270 $\mu$L) successively. The resulting slurry was filtered over a pad of Celite, followed by washing with $Et_2O$ (6 × 10 mL). The combined filtrate was dried over anhydrous $Na_2SO_4$, filtered and concentrated under reduced pressure to provide the crude dihydrolycopodine (**2**) which was used in the next step without further purification.

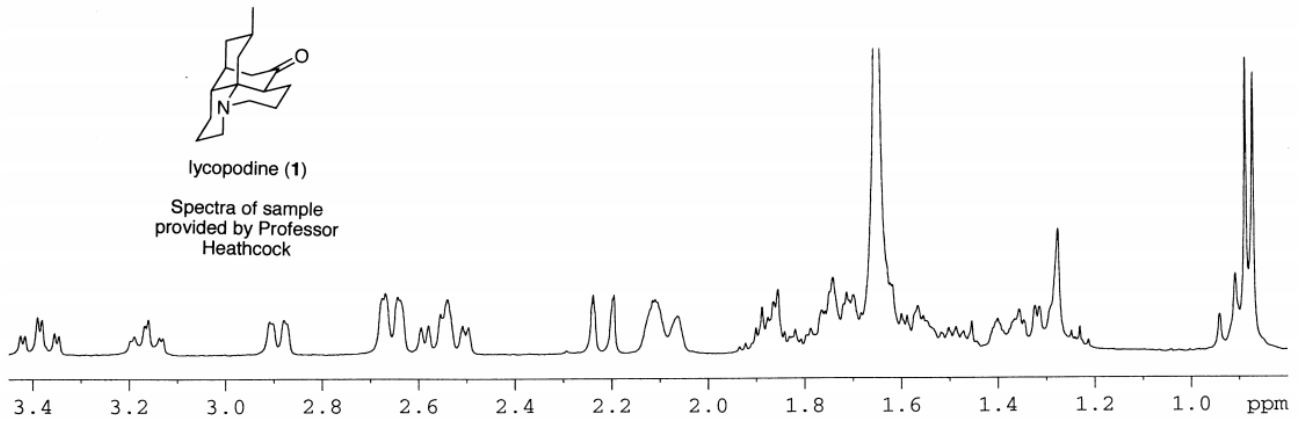
A solution of oxalyl chloride (39 $\mu$L, 0.460 mmol, 3 equiv.) in dry DCM (3 mL) at –78 ℃ was added dropwise a solution of DMSO (42 mg, 0.536 mmol, 3.5 equiv.) in DCM (1 mL). The resulting mixture was maintained at –78 ℃ for 10 min and a solution of the crude alcohol **2** (0.153 mmol,) in DCM (2 mL) was added dropwise over 3 min. The reaction was kept at –78 ℃ for an additional 40 min and then $Et_3N$ (160 $\mu$L, 1.149 mmol, 7.5 equiv.) was added dropwise over 3 min. The resulting slurry was kept at –78 ℃ for 10 min and then allowed to warm very slowly to room temperature during 6 h. The reaction was quenched with 3 mL saturated $NaHCO_3$ (aq.), and the aqueous layer was extracted with DCM (4 × 10 mL). The combined organic layers were dried with anhydrous $Na_2SO_4$, filtered and concentrated under reduced pressure. Flash chromatography of the residue over basic alumina (100–200 mesh) provided (–)-lycopodine (**1**)[2a,3] [hexanes/DCM, 1:1→0:1; 22 mg, 58% (95% brsm)] as a white solid and unoxidized (–)-dihydrolycopodine (**2**) (DCM/MeOH, 50:1→10:1; 15 mg, 39%) as a white solid.

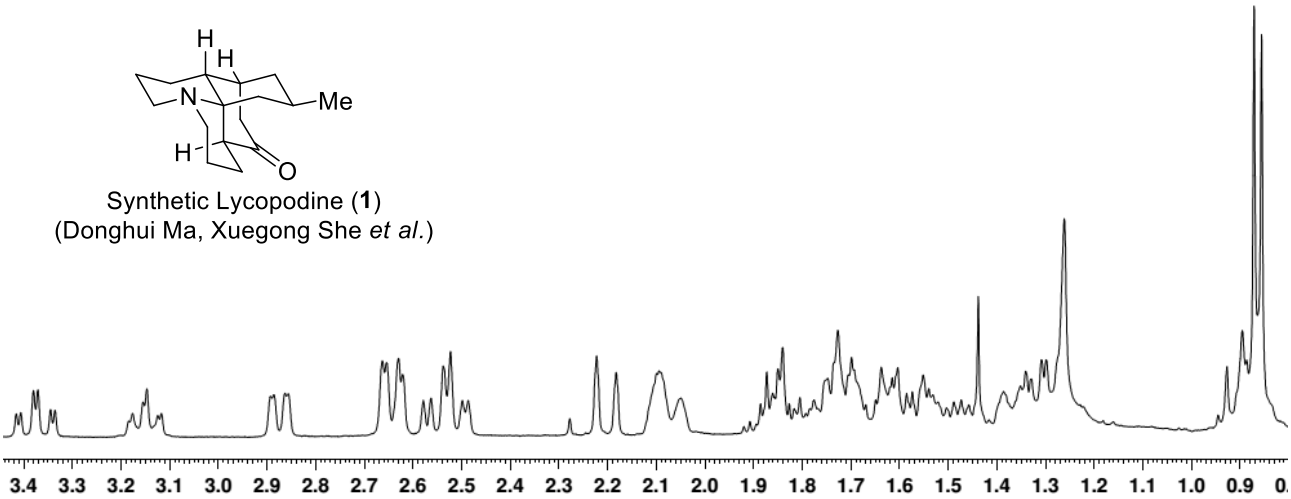
Data for (–)-lycopodine (**1**): m.p. 129–130 ℃ (recrystallized from hexanes/$Et_2O$); $[\alpha]_D^{25.9}$ = –27.3 °(*c* = 0.22, EtOH) { lit.[3b] $[\alpha]_D^{23}$ = –23.2 °(*c* = 0.22, EtOH); lit.[3c] $[\alpha]_D^{26}$ = –24.5 °(*c* = 1.10, absolute EtOH)}; IR (neat) $\nu_{max}$ = 3384, 2926, 2862, 1700, 1455, 1378, 1356, 1312, 1274, 1263, 1223, 1118, 1097, 1060, 1015, 911, 736 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 3.38 (td, *J* = 14.1, 3.7 Hz, 1H), 3.15 (td, *J* = 11.8, 3.0 Hz, 1H), 2.87 (dd, *J* = 11.9, 2.6 Hz, 1H), 2.64 (dd, *J* = 13.3, 3.4 Hz, 2H), 2.53 (td, *J* = 15.6, 5.7 Hz, 2H), 2.20 (d, *J* = 16.0 Hz, 1H), 2.10 – 2.04 (m, 2H), 1.92 – 1.20 (m, 11H), 0.95 – 0.88 (m, 1H), 0.86 (d, *J* = 6.2 Hz, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ = 213.7, 59.8, 47.2, 46.6, 45.0, 43.2, 43.0, 42.8, 42.5, 36.7, 26.1, 25.3, 25.2, 22.9, 19.5, 18.8; HRMS (ESIMS) calcd for $C_{16}H_{26}NO$: $[M+H]^+$ 248.2009; found: 248.2003.

## *Comparison of $^1$C NMR Spectrum for Synthetic Lycopodine with the Reported Spectral Data*

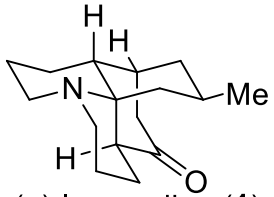
$^1$H NMR spectrum below is a copy for comparison downloaded from the article *J. Am. Chem. Soc.* **2008,** *130,* 9238–9239.[3b]



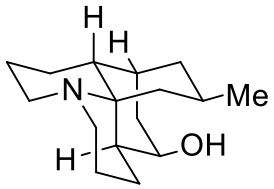
***Comparison of $^{13}$C NMR Data for Synthetic Lycopodine with the Reported Spectral Data***



(–)-lycopodine (**1**)

| Our Synthetic **1** $^{13}$C NMR Data ($CDCl_3$, 100 MHz) | Synthetic **1** $^{13}$C NMR Data by Carter[3b] ($CDCl_3$, 100 MHz) | Synthetic **1** $^{13}$C NMR Data by Kraus[3a] ($CDCl_3$, JEOl FX 90Q Spectrometer) | Natural **1** $^{13}$C NMR Data by Ayer[2a] ($CDCl_3$) |
|---|---|---|---|
| **213.7** | 213.7 | 213.3 | 213.4 |
| **77.32** | / | 77.63 | / |
| **77.00** | / | 77.06 | / |
| **76.68** | / | 77.48 | / |
| **59.8** | 59.9 | 59.7 | 59.9 |
| **47.2** | 47.2 | 47.1 | 47.8 |
| **46.6** | 46.6 | 46.6 | 47.2 |
| **45.0** | 44.9 | 44.9 | 45.5 |
| **43.2** | 43.1 | 43.2 | 43.7 |
| **43.0 (42.95)** | 42.99 | 42.8 | 43.4 |
| **42.8 (42.83)** | 42.84 | 42.7 | 43.3 |
| **42.5 (42.45)** | 42.4 | 42.4 | 43.1 |
| **36.7** | 36.7 | 36.7 | 37.3 |
| **26.1** | 26.1 | 26.1 | 26.6 |
| **25.3** | 25.3 | 25.2 | 25.8 |
| **25.2** | 25.1 | 25.1 | 25.7 |
| **22.9** | 22.9 | 22.8 | 23.3 |
| **19.5** | 19.5 | 19.5 | 20.1 |
| **18.8** | 18.8 | 18.7 | 19.3 |

***Comparison of $^{13}$C NMR Data for Synthetic Dihydrolycopodine with Natural Spectral Data***




(–)-dihydrolycopodine (**2**)

| Our Synthetic **20** $^{13}$C NMR Data ($CDCl_3$, 100 MHz) | Natural **20** $^{13}$C NMR Data by Ayer[2a] ($CDCl_3$) |
|---|---|
| **77.32** | / |
| **77.00** | / |
| **76.69** | / |
| **68.4** | 68.5 |
| **55.3** | 55.2 |
| **47.2** | 47.4 |
| **47.0** | 47.1 |
| **45.6** | 45.8 |
| **42.9** | 43.2 |
| **41.8** | 42.0 |
| **35.4** | 35.6 |
| **33.7** | 34.0 |
| **32.5** | 32.6 |
| **26.4** | 26.6 |
| **24.7** | 25.0 |
| **24.0** | 24.1 |
| **23.4** | 23.5 |
| **23.3** | 23.5 |
| **20.5** | 20.7 |

## References

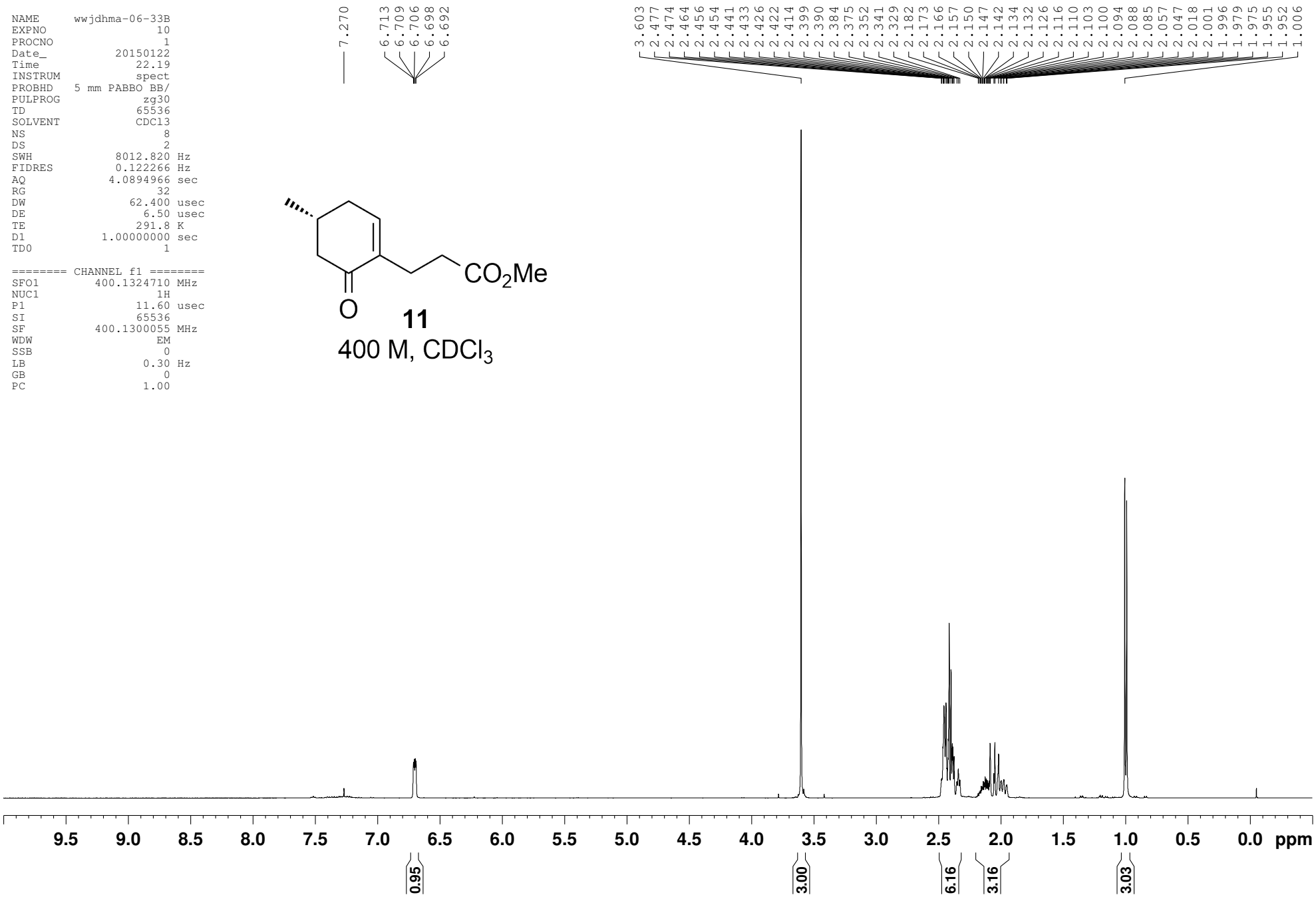
(1) (a) Reusch, W.; Johnson, C. K. *J. Org. Chem.* **1963**, *28*, 2557–2560. (b) Katauhara, J. *J. Org. Chem.* **1967**, *32*, 797–799. (c) Caine D.; Procter K.; Cassell R. A.; *J. Org. Chem.* **1984**, *49*, 2647–2648. (d) Mutti S.; Daubié C.; Decalogne F.; Fournier R.; Rossi P. *Tetrahedron Lett.* **1996**, *37*, 3125–3128. (e) Kozak, J. A.; Dake, G. R. *Angew. Chem., Int. Ed.* **2008**, *47*, 4221–4223.

(2) (a) Nakashima, T. T.; Singer, P. P.; Browne, L. M.; Ayer, W. A. *Can. J. Chem.* **1975**, *53*, 1936–1942. (b) Ayer, W. A.; Berezowsky, J. A.; Iverach, G. G. *Tetrahedron* **1962**, *18*, 567–573. (c) Johns, S. R.; Lamberton, J. A.; Sioumis, A. A. *Aust. J. Chem.* **1969**, *22*, 1317.

(3) (a) Kraus, G. A.; Hon, Y. S. *Heterocycles.* **1987**, *25*, 377–386. (b) Yang, H.; Carter, R. G.; Zakharov, L. N. *J. Am. Chem. Soc.* **2008**, *130*, 9238–9239. (c) B. Douglas, B.; Lewis, D. G.; Marion, L. *Can. J. Chem.* **1953**, *31*, 272–276.

# Copies of $^{1}$H and $^{13}$C NMR Spectra

**1.** ***See the next page.***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EXPNO 10
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Time 22.19
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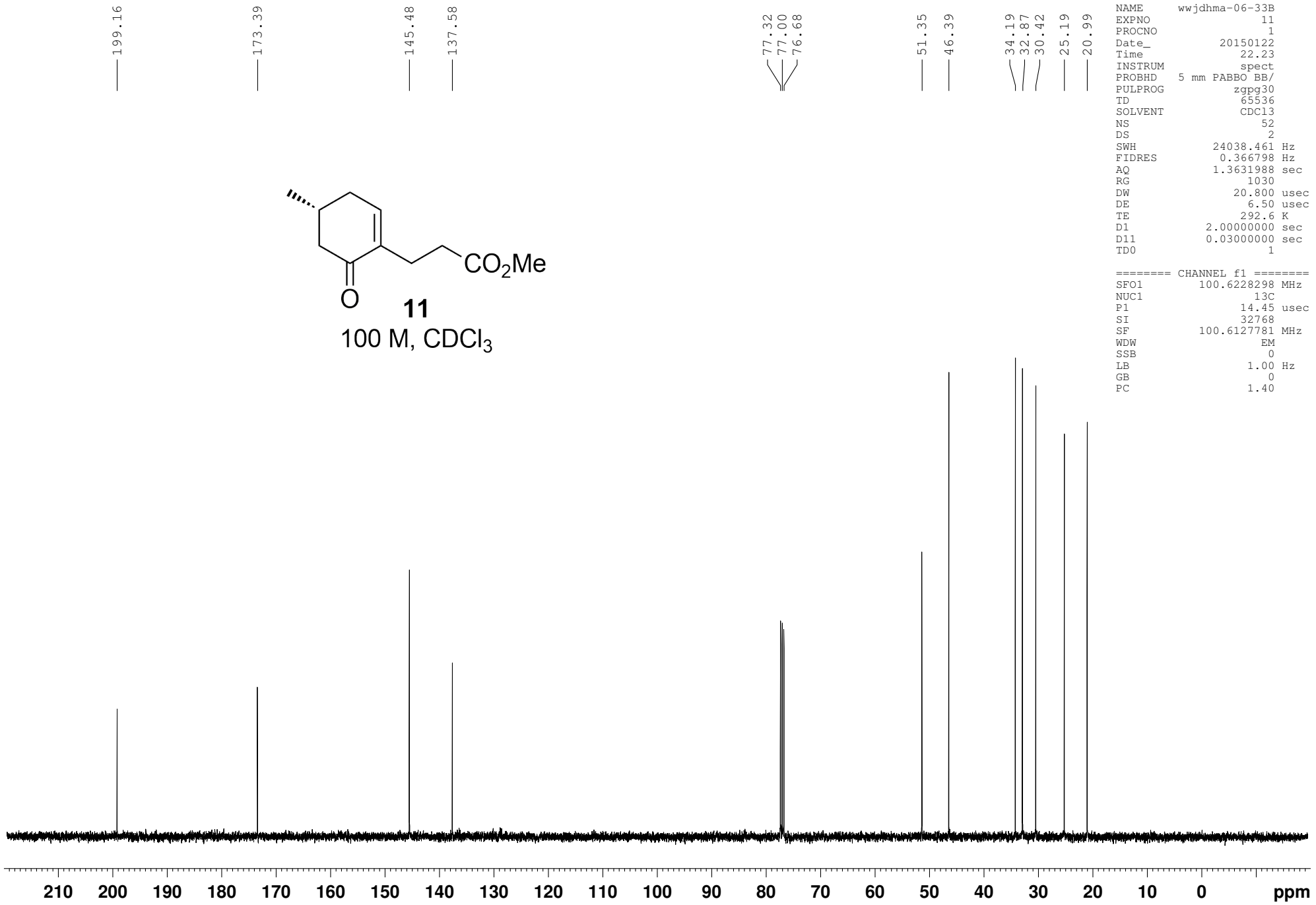
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 32
DW 62.400 usec
DE 6.50 usec
TE 291.8 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1324710 MHz
NUC1 1H
P1 11.60 usec
SI 65536
SF 400.1300055 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
7.270
6.713
6.709
6.706
6.698
6.692
3.603
2.477
2.474
2.464
2.456
2.454
2.441
2.433
2.426
2.422
2.414
2.399
2.390
2.384
2.375
2.352
2.341
2.329
2.182
2.173
2.166
2.157
2.150
2.147
2.142
2.134
2.132
2.126
2.116
2.110
2.103
2.100
2.094
2.088
2.085
2.057
2.047
2.018
2.001
1.996
1.979
1.975
1.955
1.952
1.006
CO2Me
O
11
400 M, CDCl3
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
0.95
3.00
6.16
3.16
3.03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173.39
145.48
137.58
77.32
77.00
76.68
51.35
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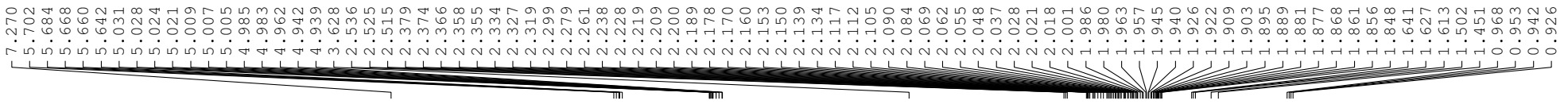
32.87
30.42
25.19
20.99
NAME wwjdhma-06-33B
EXPNO 11
PROCNO 1
Date_ 20150122
Time 22.23
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 52
DS 2
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 1030
DW 20.800 usec
DE 6.50 usec
TE 292.6 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 100.6228298 MHz
NUC1 13C
P1 14.45 usec
SI 32768
SF 100.6127781 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
CO2Me
O
11
100 M, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

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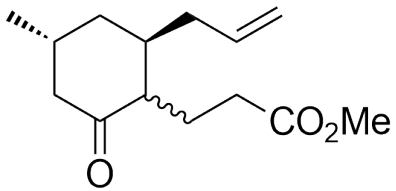
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                    32
DW                62.400 usec
DE                 6.50 usec
TE                2926.0 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         400.1324710 MHz
NUC1                  1H
P1                14.10 usec
SI                 65536
SF           400.1300055 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

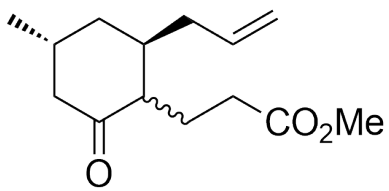



**S-2** (d.r.=1:1)
400 M, $CDCl_3$

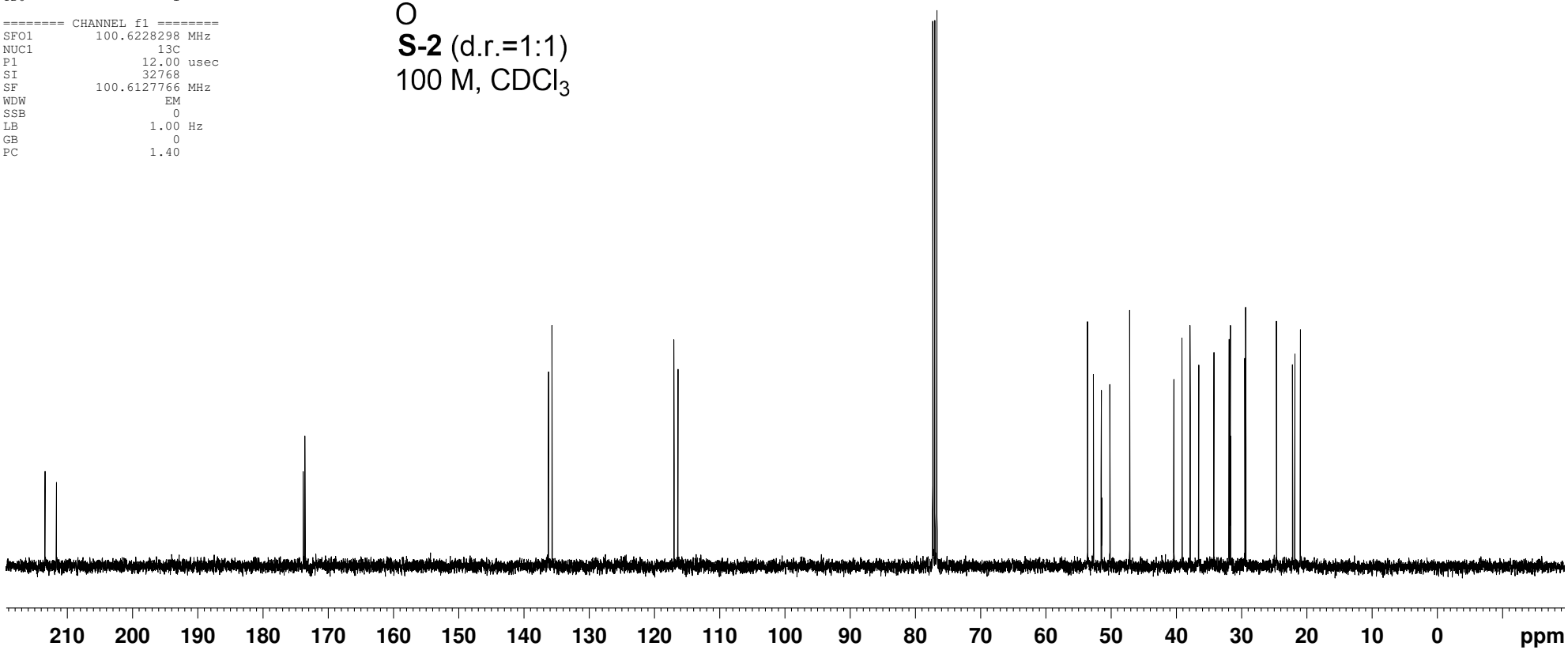
213.38
211.64
173.81
173.54
136.22
135.68
116.98
116.36
77.31
77.00
76.68
53.59
52.69
51.49
51.43
50.16
47.13
40.36
39.11
37.86
36.54
34.22
31.89
31.70
31.66
29.48
29.32
24.63
22.16
21.81
20.97

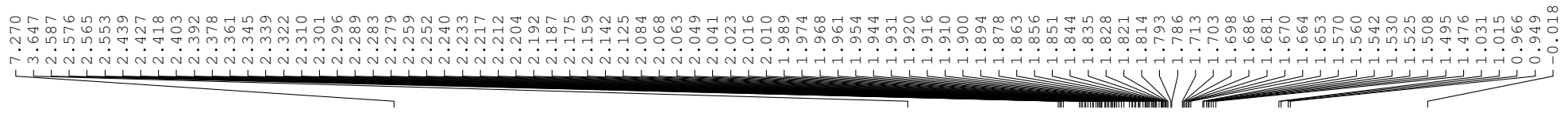
```
NAME      wwjdhma-06-34B
EXPNO                12
PROCNO                1
Date_          20150123
Time              15.54
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   60
DS                    2
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631988 sec
RG                  362
DW               20.800 usec
DE                6.50 usec
TE               2937.0 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        100.6228298 MHz
NUC1                13C
P1                12.00 usec
SI                32768
SF          100.6127766 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```




**S-2** (d.r.=1:1)
100 M, $CDCl_3$






```
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PROCNO                   1
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Time                 22.21
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      16
DS                       2
SWH               8012.820 Hz
FIDRES            0.122266 Hz
AQ                4.0894966 sec
RG                     90.5
DW                  62.400 usec
DE                   6.50 usec
TE                   294.5 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1           400.1324710 MHz
NUC1                    1H
P1                   10.92 usec
SI                   65536
SF             400.1300057 MHz
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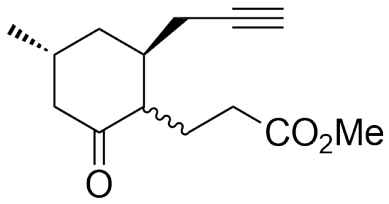
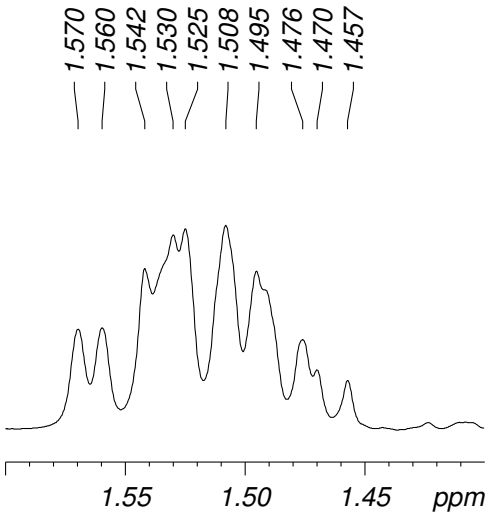
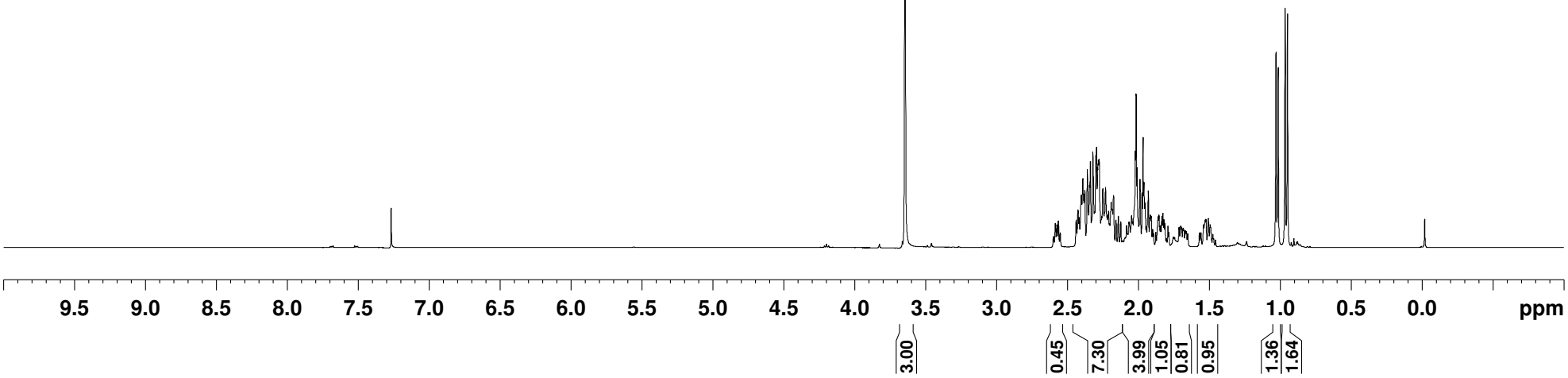
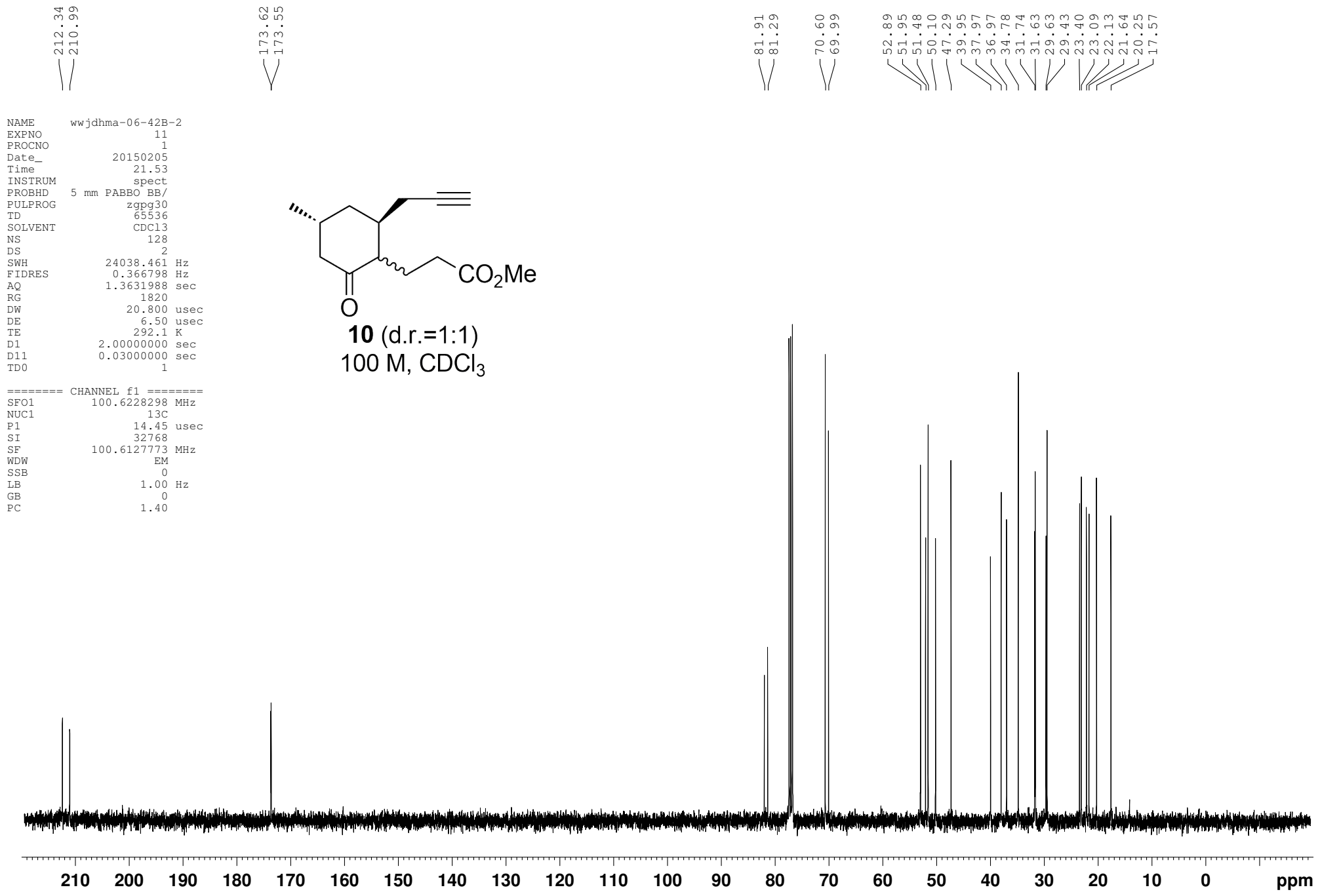
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```




**10** (d.r.=1:1)
400 M, $CDCl_3$




212.34
210.99
173.62
173.55
81.91
81.29
70.60
69.99
52.89
51.95
51.48
50.10
47.29
39.95
37.97
36.97
34.78
31.74
31.63
29.63
29.43
23.40
23.09
22.13
21.64
20.25
17.57
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EXPNO 11
PROCNO 1
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Time 21.53
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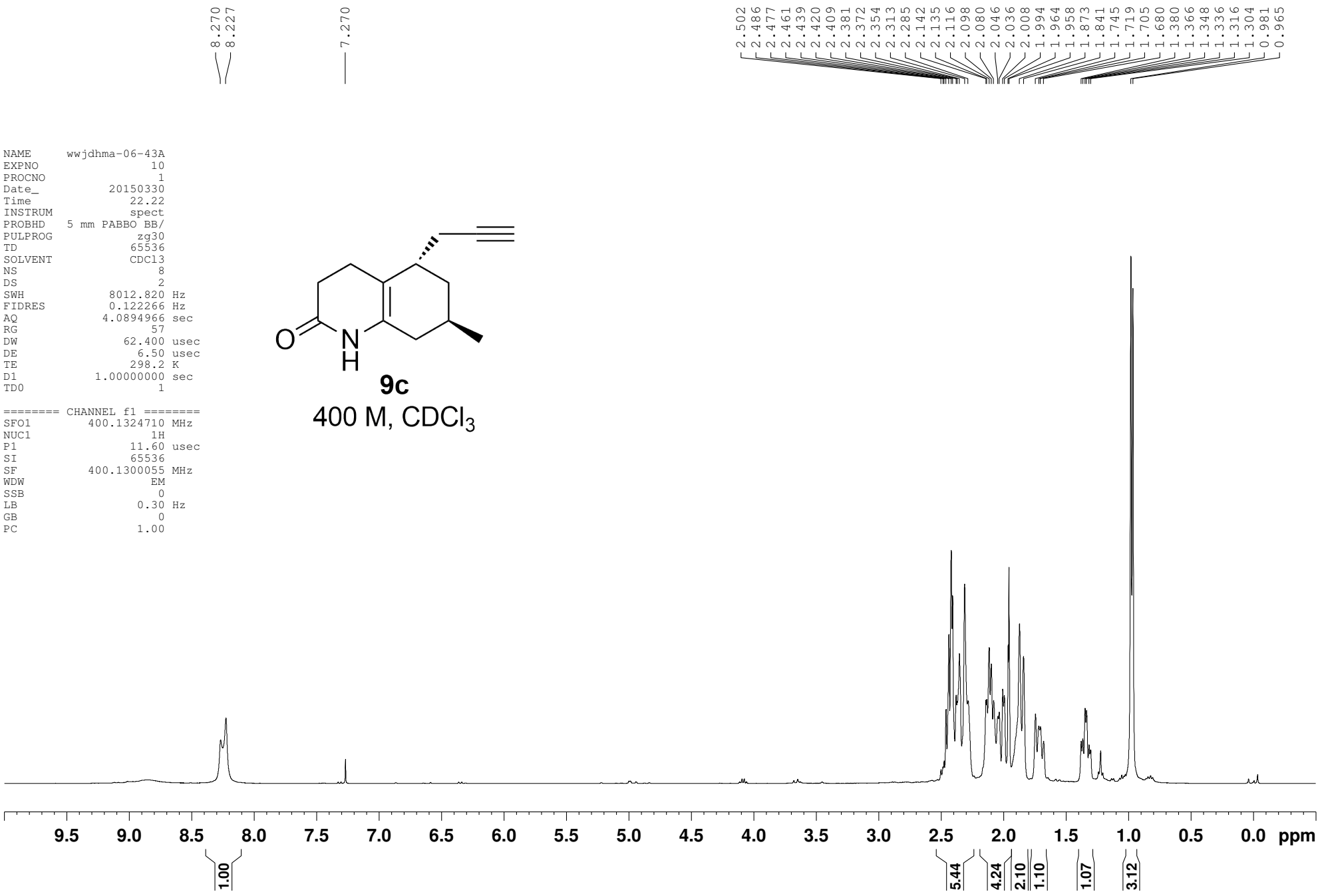
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 128
DS 2
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 1820
DW 20.800 usec
DE 6.50 usec
TE 292.1 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 100.6228298 MHz
NUC1 13C
P1 14.45 usec
SI 32768
SF 100.6127773 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
CO2Me
O
10 (d.r.=1:1)
100 M, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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8.227
7.270
2.502
2.486
2.477
2.461
2.439
2.420
2.409
2.381
2.372
2.354
2.313
2.285
2.142
2.135
2.116
2.098
2.080
2.046
2.036
2.008
1.994
1.964
1.958
1.873
1.841
1.745
1.719
1.705
1.680
1.380
1.366
1.348
1.336
1.316
1.304
0.981
0.965
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EXPNO 10
PROCNO 1
Date_ 20150330
Time 22.22
INSTRUM spect
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PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 57
DW 62.400 usec
DE 6.50 usec
TE 298.2 K
D1 1.00000000 sec
TD0 1
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SFO1 400.1324710 MHz
NUC1 1H
P1 11.60 usec
SI 65536
SF 400.1300055 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
O
N
H
9c
400 M, CDCl3
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
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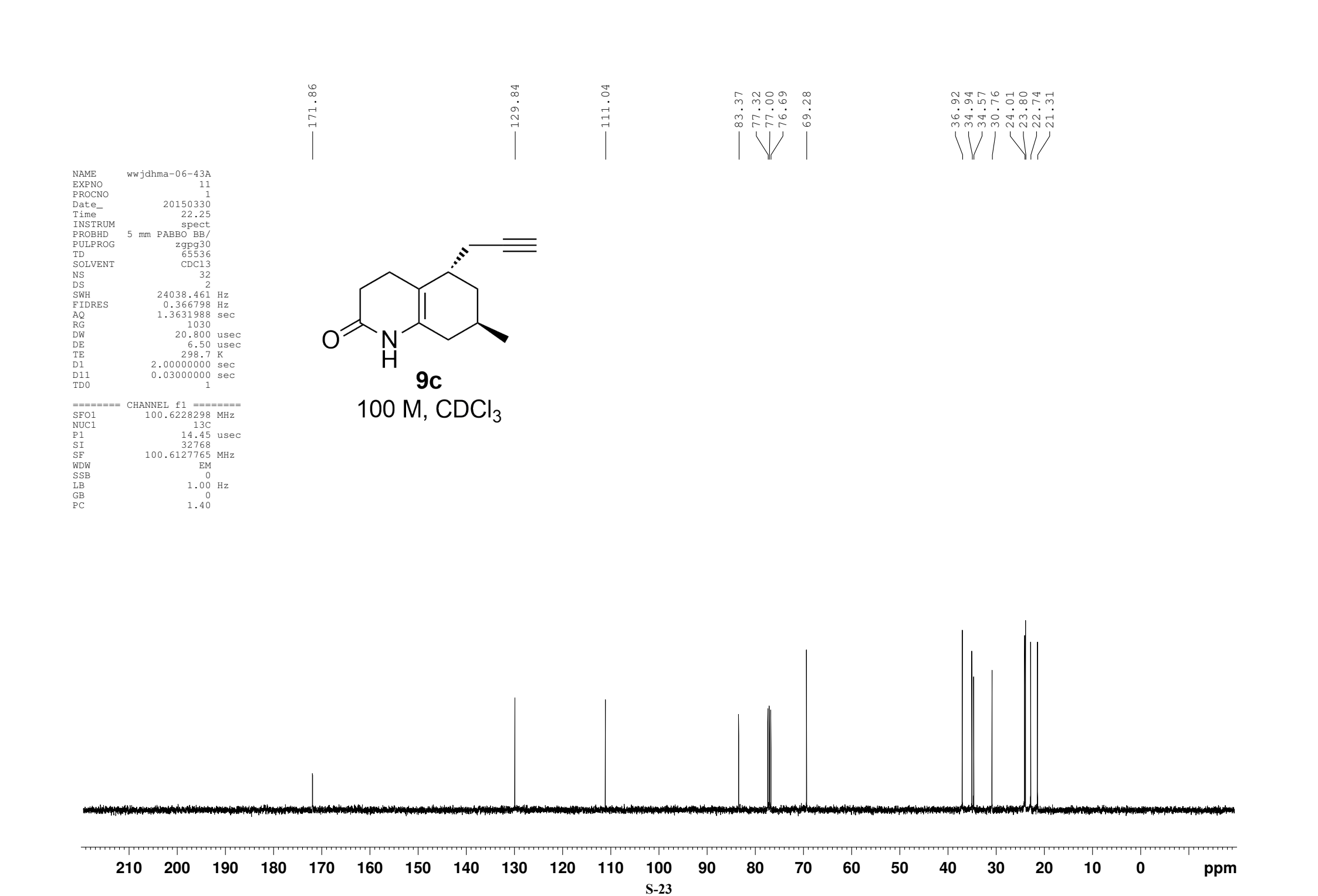
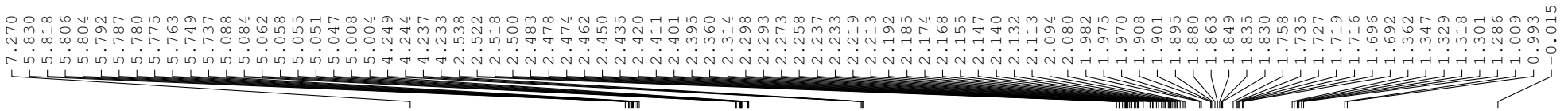
5.44
4.24
2.10
1.10
1.07
3.12


171.86
129.84
111.04
83.37
77.32
77.00
76.69
69.28
36.92
34.94
34.57
30.76
24.01
23.80
22.74
21.31
NAME wwjdhma-06-43A
EXPNO 11
PROCNO 1
Date_ 20150330
Time 22.25
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 32
DS 2
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 1030
DW 20.800 usec
DE 6.50 usec
TE 298.7 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 100.6228298 MHz
NUC1 13C
P1 14.45 usec
SI 32768
SF 100.6127765 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
O
N
H
9c
100 M, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm




```
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PROCNO                1
Date_          20150425
Time              23.46
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PROBHD   5 mm PABBO BB/
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            8012.820 Hz
FIDRES        0.122266 Hz
AQ            4.0894966 sec
RG                71.8
DW               62.400 usec
DE                6.50 usec
TE               291.9 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1         400.1324710 MHz
NUC1                 1H
P1                10.79 usec
SI                65536
SF           400.1300057 MHz
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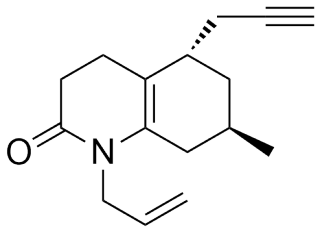
LB                 0.30 Hz
GB                    0
PC                 1.00
```




**9a**

400 M, $CDCl_3$

```
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PROCNO                 1
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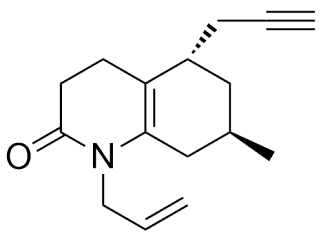
Time               23.51
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   60
DS                    2
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631988 sec
RG                 2050
DW               20.800 usec
DE                6.50 usec
TE               293.0 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1

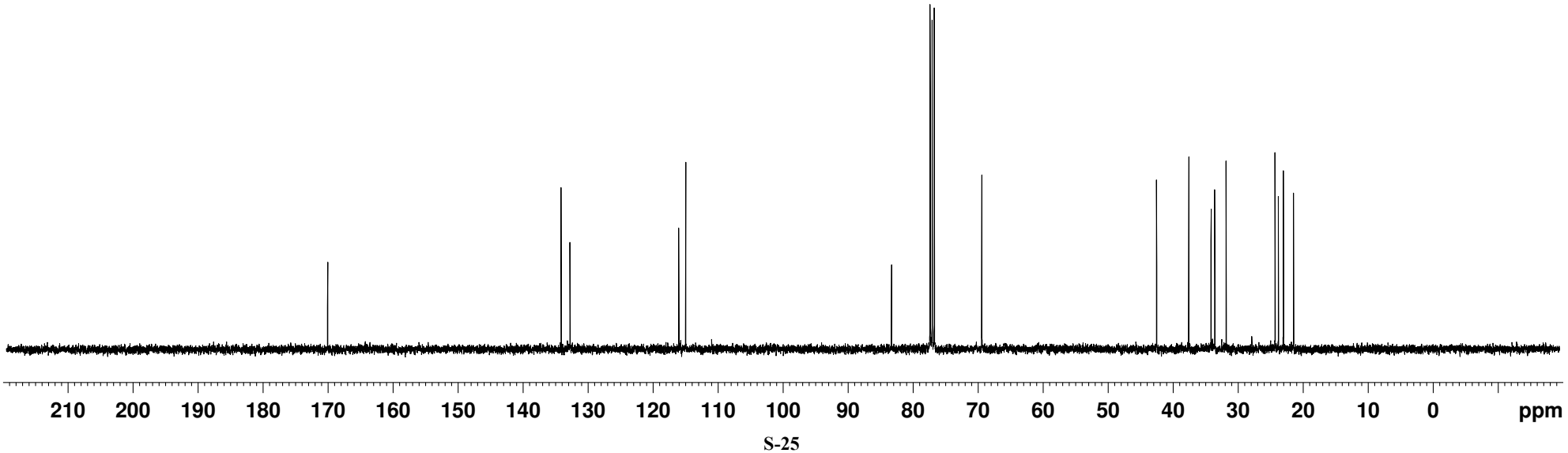
======== CHANNEL f1 ========
SFO1        100.6228298 MHz
NUC1                13C
P1                12.00 usec
SI                32768
SF          100.6127759 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

170.01
134.11
132.73
115.99
114.92
83.25
77.32
77.00
76.69
69.37
42.48
37.53
34.11
33.53
31.79
24.26
23.75
22.98
21.42




**9a**

100 M, $CDCl_3$



```
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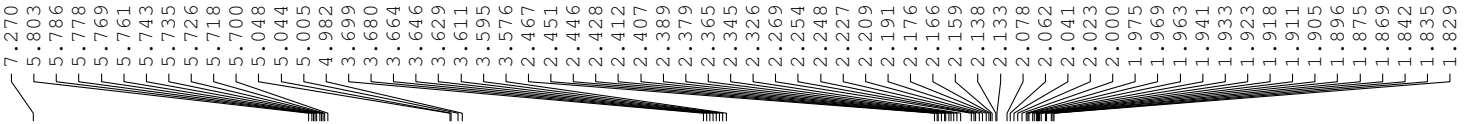
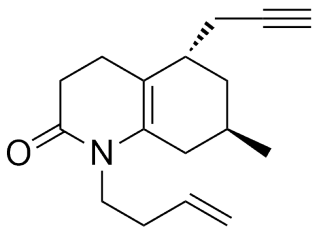
PROCNO                 1
Date_           20150611
Time               22.03
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                    64
DW                62.400 usec
DE                 6.50 usec
TE                294.5 K
D1           1.00000000 sec
TD0                    1

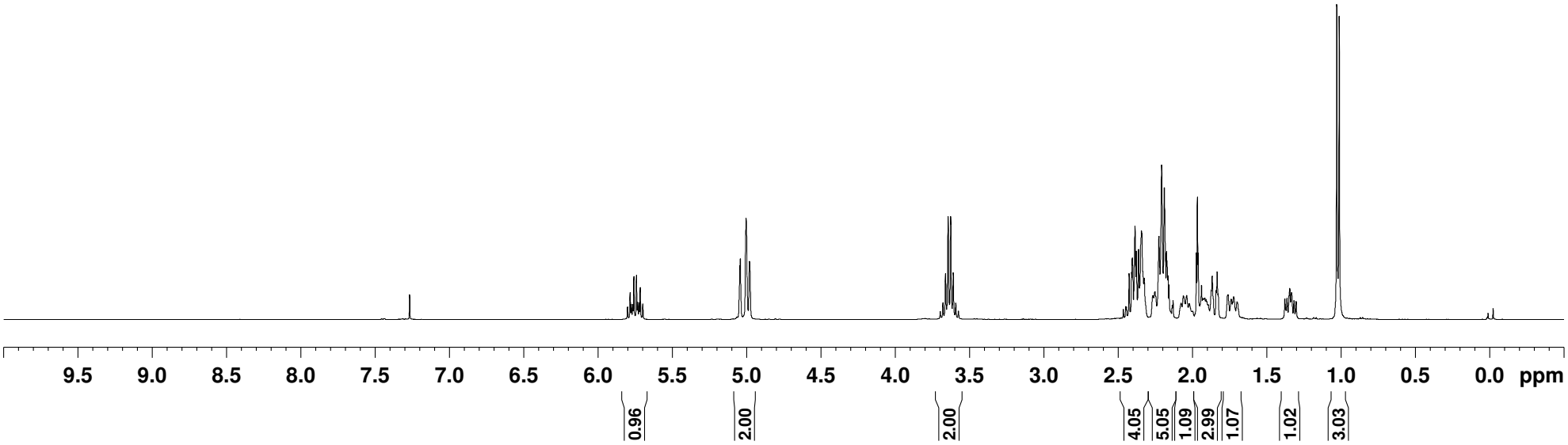
======== CHANNEL f1 ========
SFO1         400.1324710 MHz
NUC1                 1H
P1                10.92 usec
SI                65536
SF           400.1300058 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```




**9b**

400 M, $CDCl_3$

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PROCNO                 1
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Time               22.10
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG            zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   108
DS                     2
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631988 sec
RG                  1290
DW                20.800 usec
DE                 6.50 usec
TE                295.4 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         100.6228298 MHz
NUC1                13C
P1                14.70 usec
SI                32768
SF           100.6127758 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```
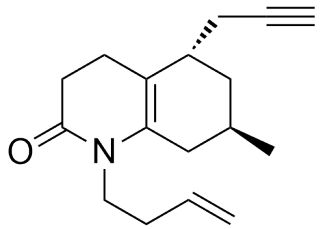
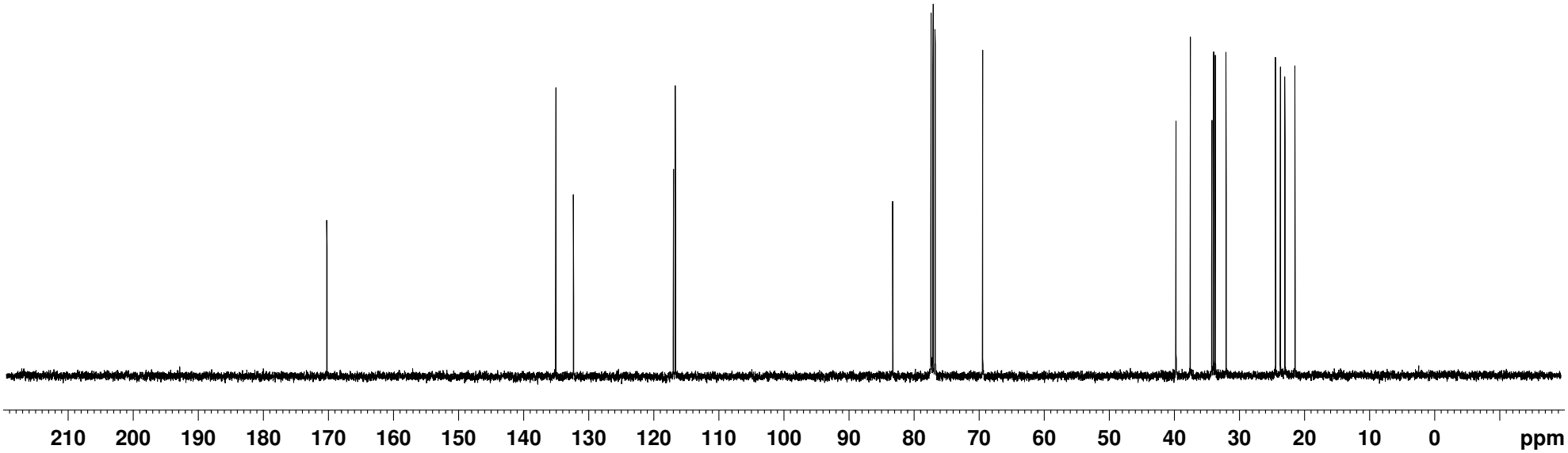
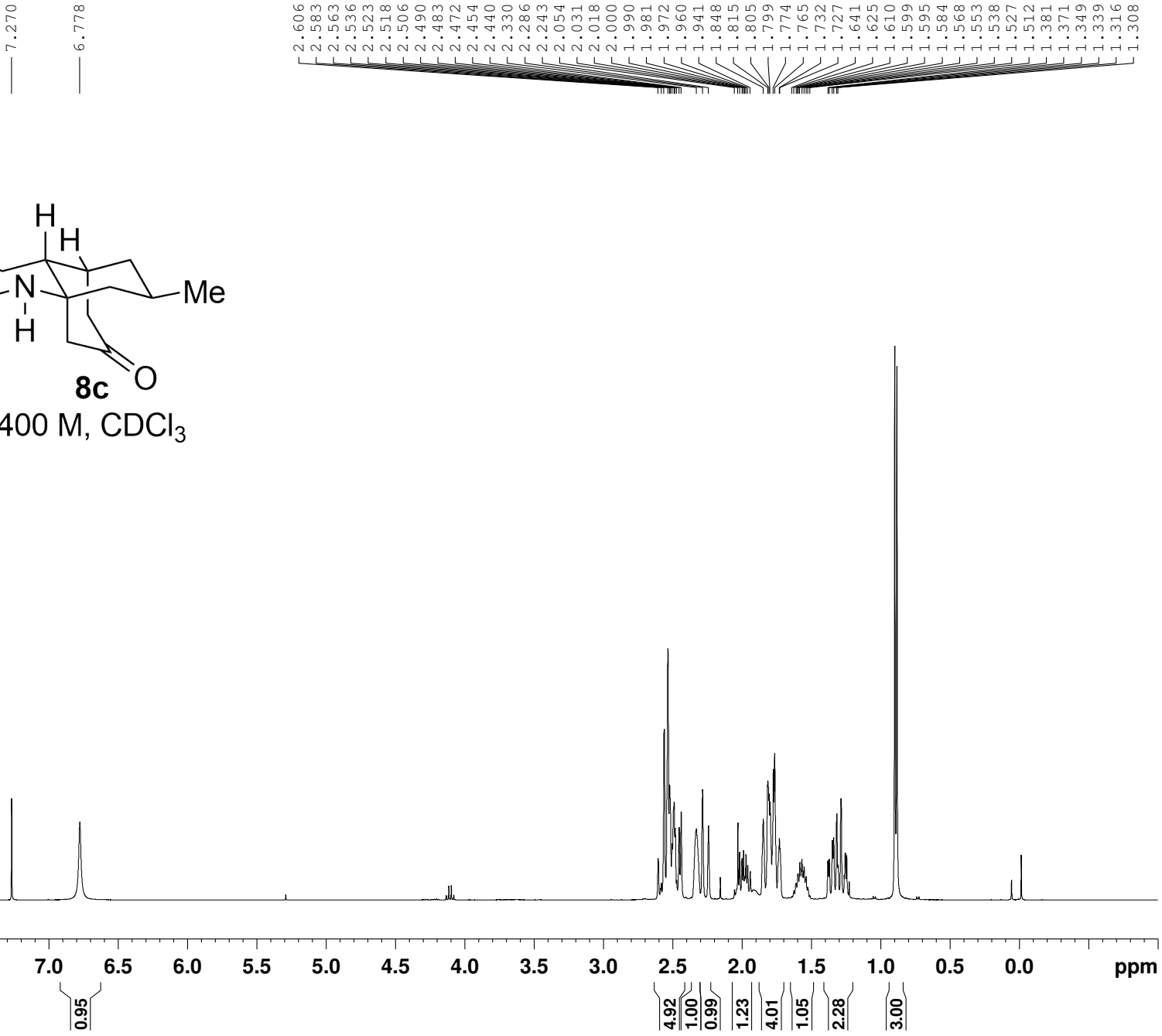




**9b**

100 M, $CDCl_3$



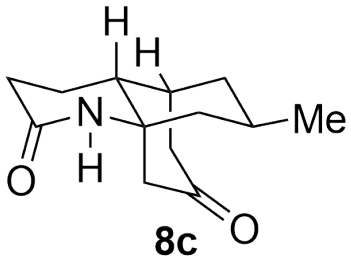

7.270
6.778
2.606
2.583
2.563
2.536
2.523
2.518
2.506
2.490
2.483
2.472
2.454
2.440
2.330
2.286
2.243
2.054
2.031
2.018
2.000
1.990
1.981
1.972
1.960
1.941
1.848
1.815
1.805
1.799
1.774
1.765
1.732
1.727
1.641
1.625
1.610
1.599
1.595
1.584
1.568
1.553
1.538
1.527
1.512
1.381
1.371
1.349
1.339
1.316
1.308
NAME wwjdhma-06-44A
EXPNO 10
PROCNO 1
Date_ 20150402
Time 22.07
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 128
DW 62.400 usec
DE 6.50 usec
TE 296.5 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1324710 MHz
NUC1 1H
P1 11.60 usec
SI 65536
SF 400.1300055 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
H
H
N
H
O
Me
O
8c
400 M, CDCl3
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
0.95
4.92
1.00
0.99
1.23
4.01
1.05
2.28
3.00

208.74

77.31
77.00
76.68

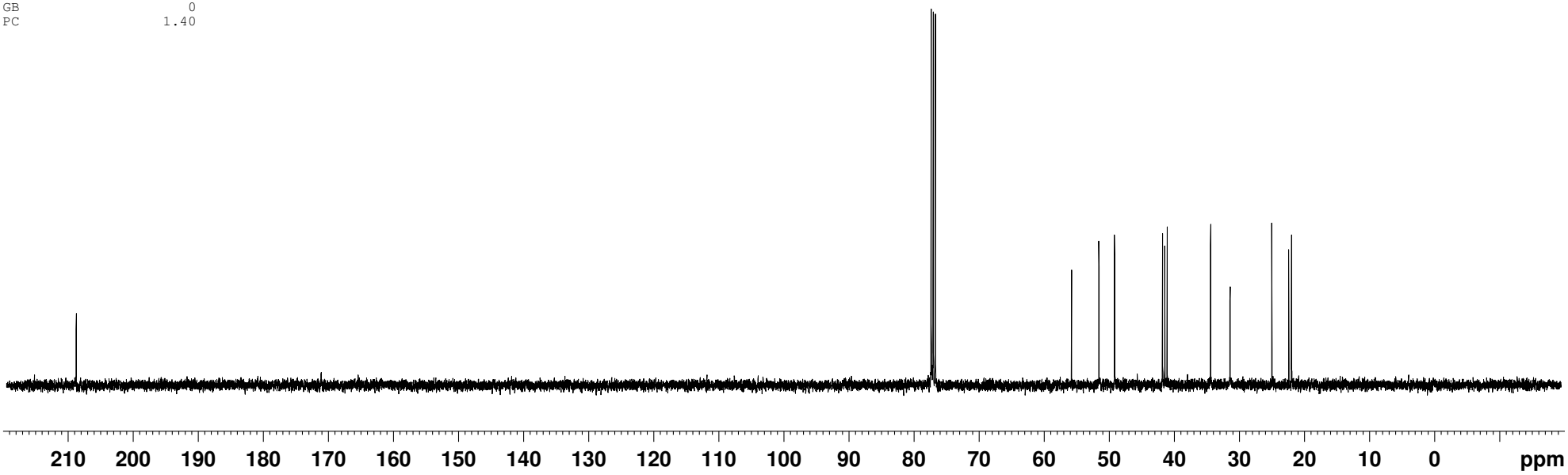
55.73
51.54
49.13
41.76
41.43
41.04
34.37
31.38
24.96
22.36
21.93

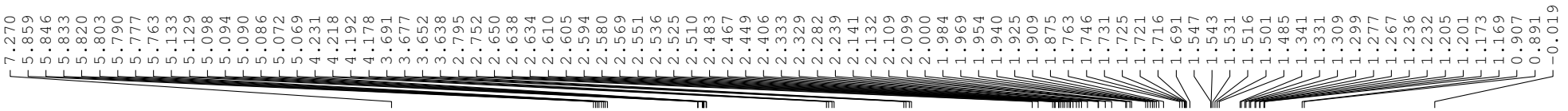
```
NAME      wwjdhma-06-44A
EXPNO                 11
PROCNO                 1
Date_           20150402
Time               22.14
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  105
DS                    2
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631988 sec
RG                 2050
DW               20.800 usec
DE                6.50 usec
TE                297.3 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        100.6228298 MHz
NUC1                13C
P1                14.45 usec
SI                32768
SF          100.6127743 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```



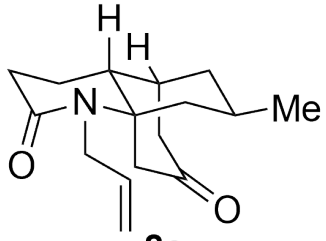

**8c**

100 M, $CDCl_3$



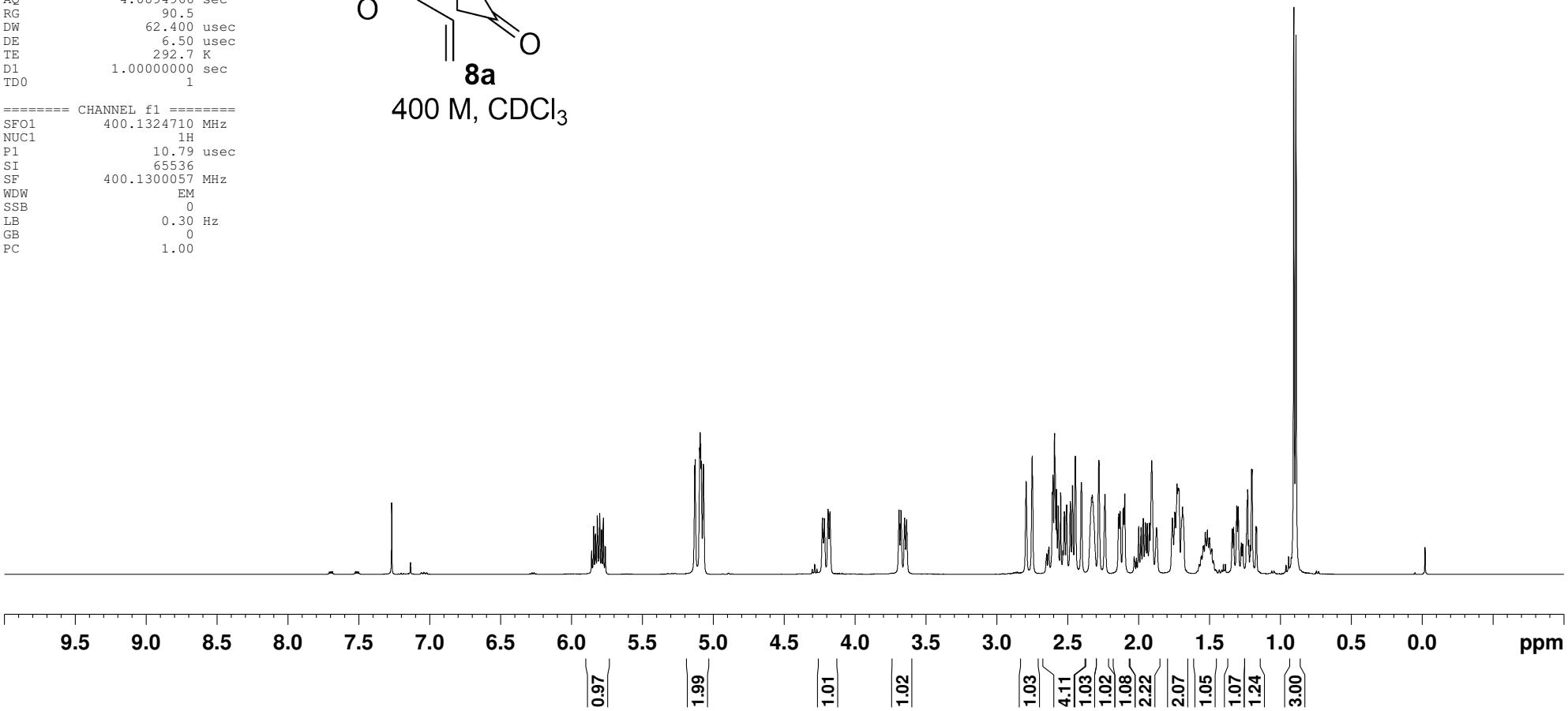


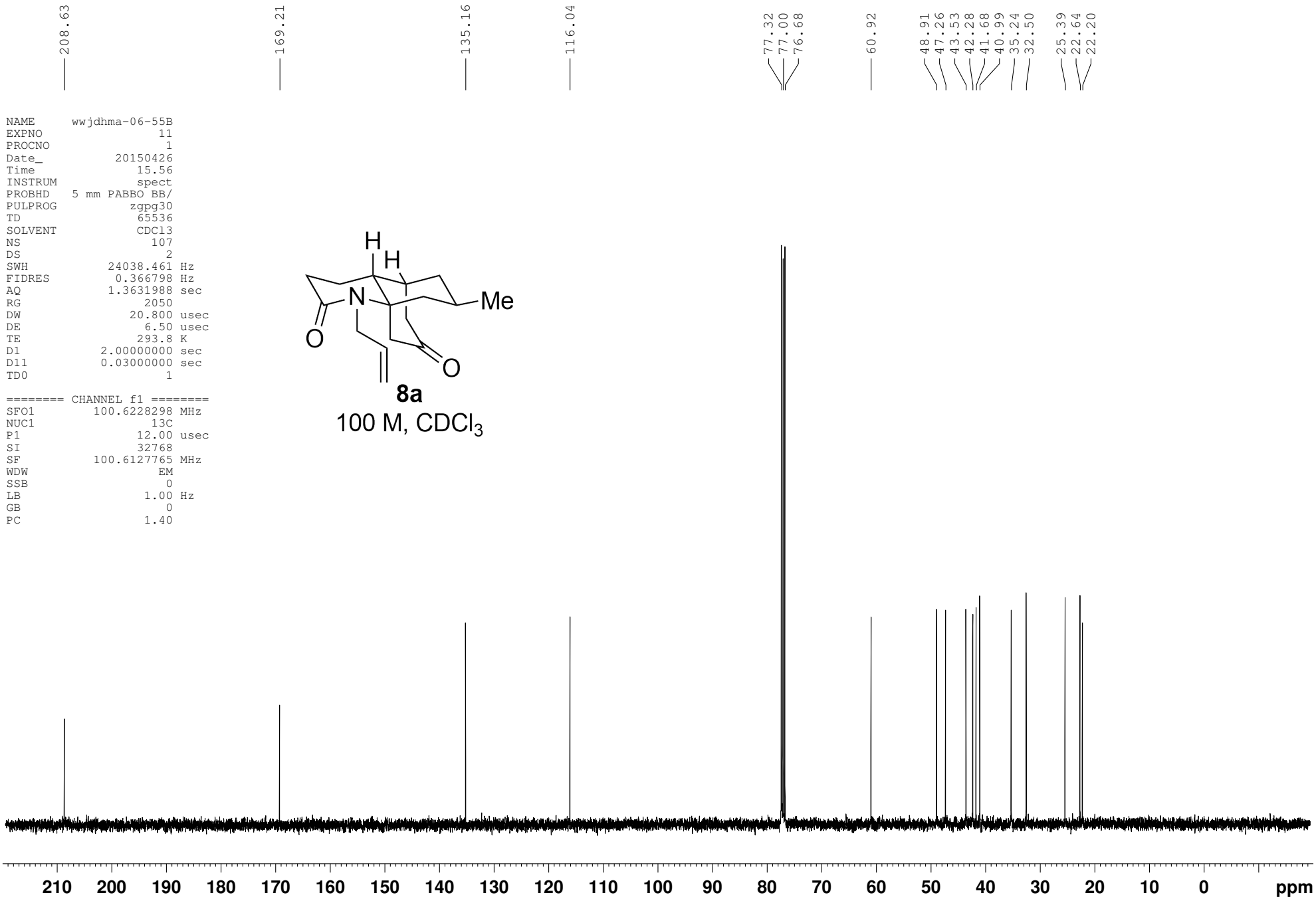

```
NAME      wwjdhma-06-55B
EXPNO                10
PROCNO                1
Date_          20150426
Time              15.49
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            8012.820 Hz
FIDRES        0.122266 Hz
AQ            4.0894966 sec
RG                90.5
DW              62.400 usec
DE               6.50 usec
TE              292.7 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        400.1324710 MHz
NUC1                1H
P1                10.79 usec
SI                65536
SF          400.1300057 MHz
WDW                 EM
SSB                  0
LB                0.30 Hz
GB                   0
PC                1.00
```

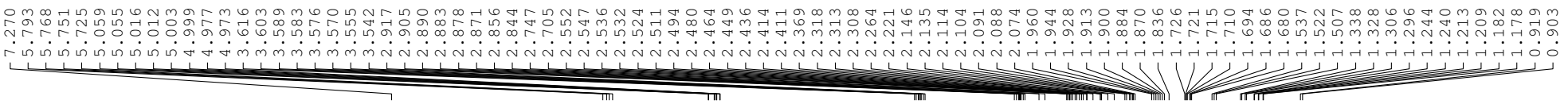



**8a**

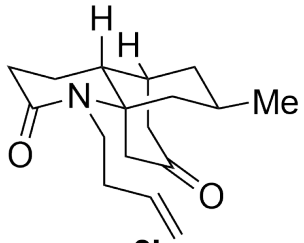
400 M, $CDCl_3$




208.63
169.21
135.16
116.04
77.32
77.00
76.68
60.92
48.91
47.26
43.53
42.28
41.68
40.99
35.24
32.50
25.39
22.64
22.20
NAME wwjdhma-06-55B
EXPNO 11
PROCNO 1
Date_ 20150426
Time 15.56
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 107
DS 2
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 2050
DW 20.800 usec
DE 6.50 usec
TE 293.8 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 100.6228298 MHz
NUC1 13C
P1 12.00 usec
SI 32768
SF 100.6127765 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
H
H
N
Me
O
O
8a
100 M, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm




```
NAME      wwjdhma-06-67A
EXPNO                 11
PROCNO                 1
Date_           20150525
Time               22.06
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ              4.0894966 sec
RG                  71.8
DW                62.400 usec
DE                 6.50 usec
TE                294.3 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         400.1324710 MHz
NUC1                   1H
P1                 10.92 usec
SI                 65536
SF           400.1300057 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

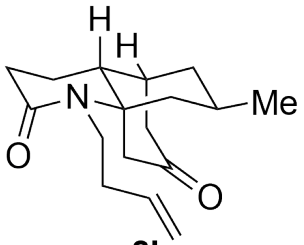



**8b**

400 M, $CDCl_3$

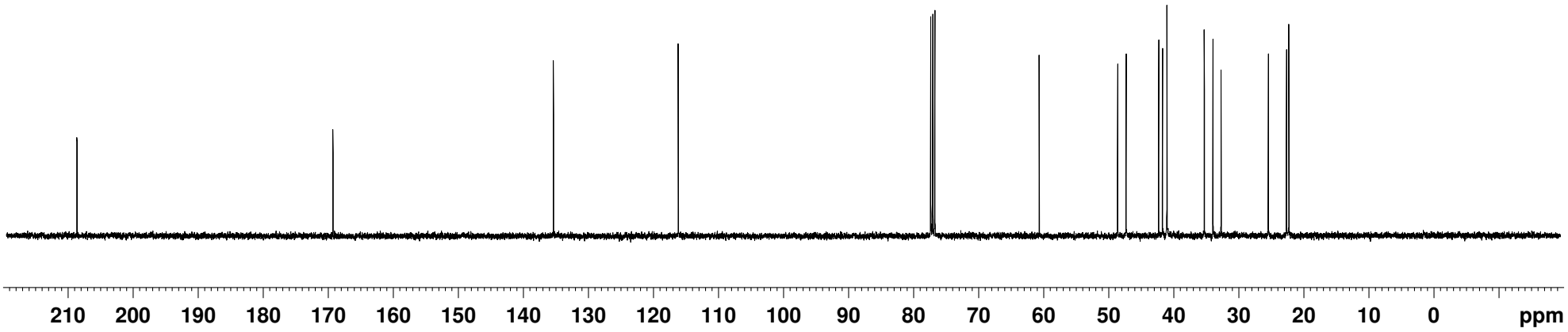
208.55
169.25
135.34
116.15
77.32
77.00
76.68
60.64
48.57
47.26
42.26
41.67
41.00
40.98
35.23
33.90
32.66
25.39
22.60
22.23

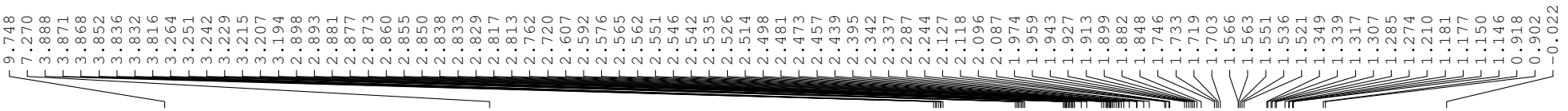
```
NAME      wwjdhma-06-67A
EXPNO                12
PROCNO                1
Date_          20150525
Time              22.12
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG         zgpg30
TD                65536
SOLVENT           CDCl3
NS                   90
DS                    2
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ             1.3631988 sec
RG                 812
DW                20.800 usec
DE                 6.50 usec
TE                295.1 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1         100.6228298 MHz
NUC1                13C
P1                14.70 usec
SI                32768
SF           100.6127788 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```



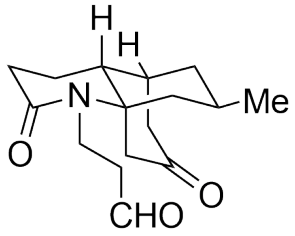

**8b**

100 M, $CDCl_3$



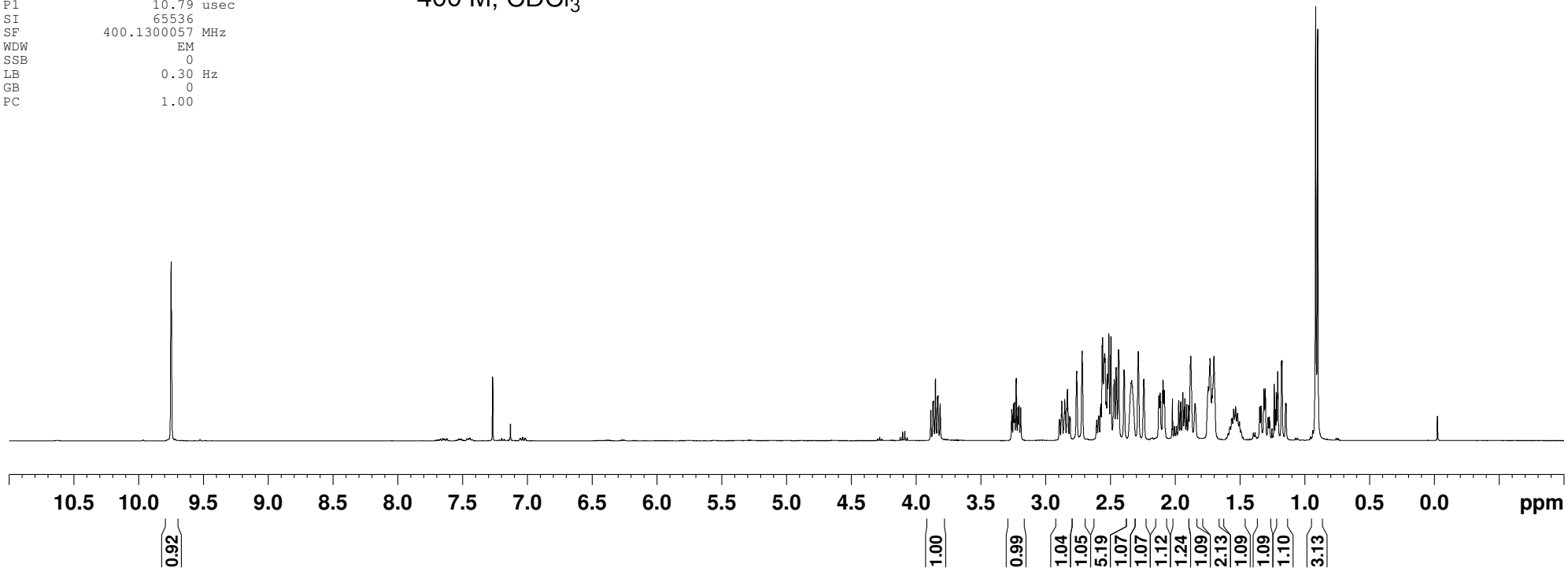



```
NAME      wwjdhma-06-71A
EXPNO                 10
PROCNO                 1
Date_           20150603
Time               14.09
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ              4.0894966 sec
RG                   128
DW                62.400 usec
DE                 6.50 usec
TE                294.1 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1          400.1324710 MHz
NUC1                  1H
P1                 10.79 usec
SI                 65536
SF            400.1300057 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```



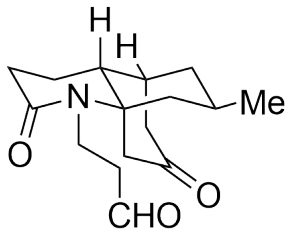

**15**

400 M, $CDCl_3$



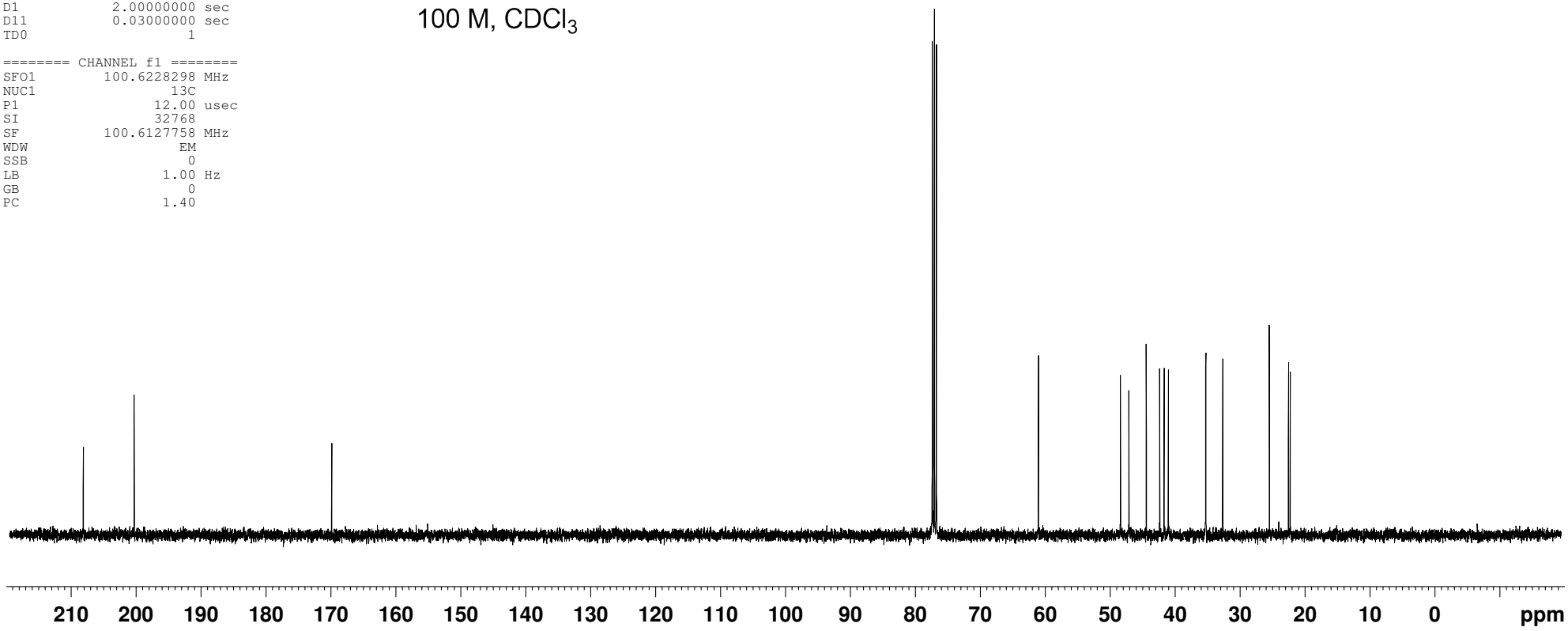
208.08
200.25
169.82
77.32
77.00
76.68
60.97
48.36
47.06
44.37
42.32
41.62
40.95
35.23
35.18
32.58
25.41
22.48
22.20

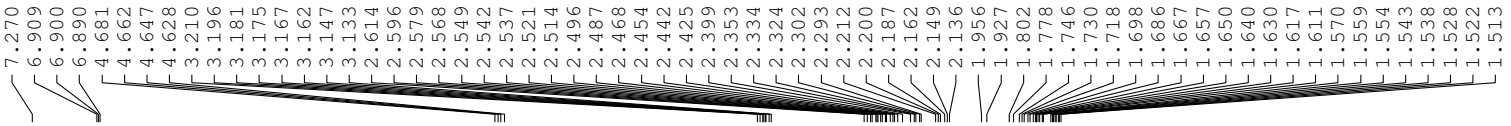
```
NAME      wwjdhma-06-71A
EXPNO                 11
PROCNO                 1
Date_           20150603
Time               14.11
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  105
DS                    2
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631988 sec
RG                 2050
DW                20.800 usec
DE                 6.50 usec
TE                294.5 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        100.6228298 MHz
NUC1                13C
P1                12.00 usec
SI                32768
SF          100.6127758 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```



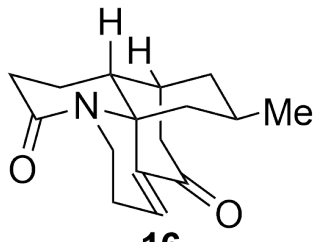

**15**

100 M, $CDCl_3$



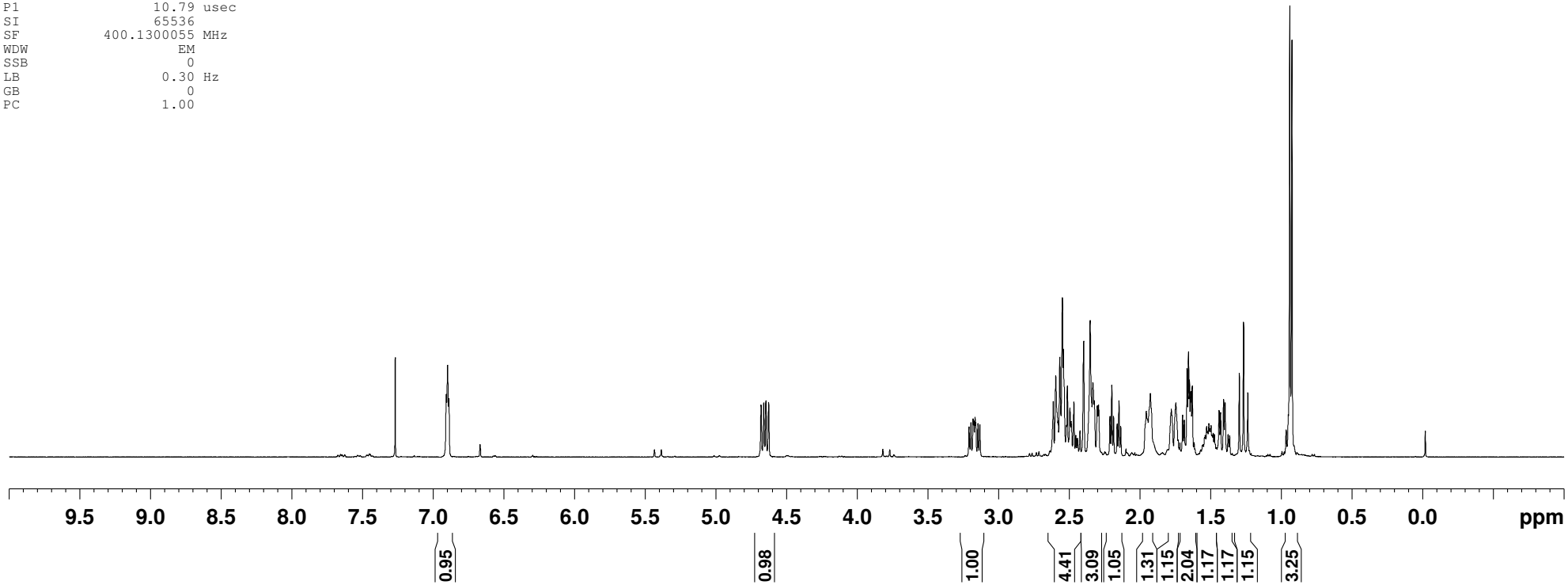



```
NAME      wwjdhma-06-79A-2
EXPNO                   10
PROCNO                   1
Date_             20150628
Time                 15.30
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      16
DS                       2
SWH               8012.820 Hz
FIDRES            0.122266 Hz
AQ                4.0894966 sec
RG                     144
DW                  62.400 usec
DE                   6.50 usec
TE                  294.9 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1            400.1324710 MHz
NUC1                    1H
P1                   10.79 usec
SI                   65536
SF              400.1300055 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```



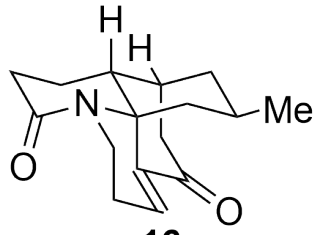

**16**

400 M, $CDCl_3$



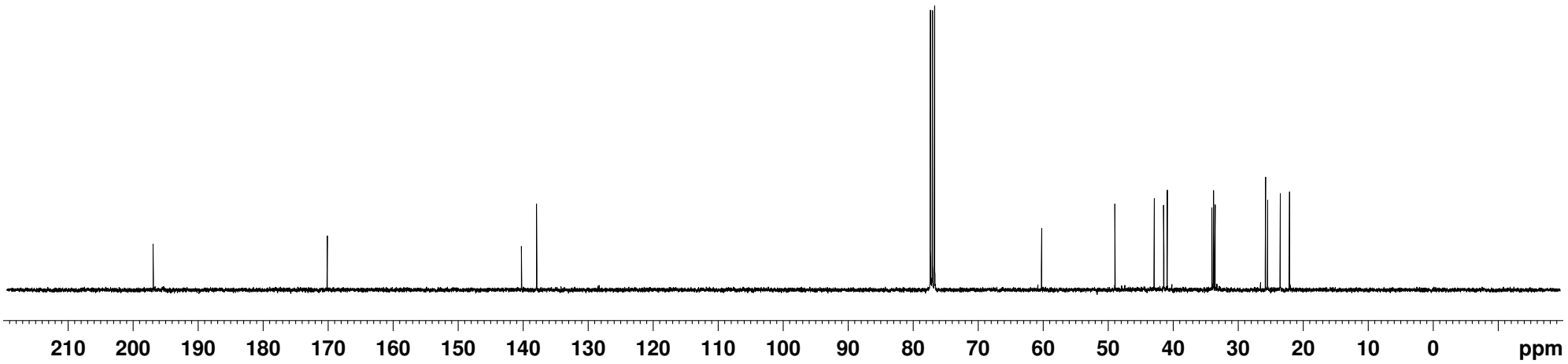
196.91
170.12
140.24
137.91
77.31
77.00
76.68
60.21
48.93
42.87
41.42
40.87
34.00
33.75
33.52
25.76
25.42
23.49
22.06

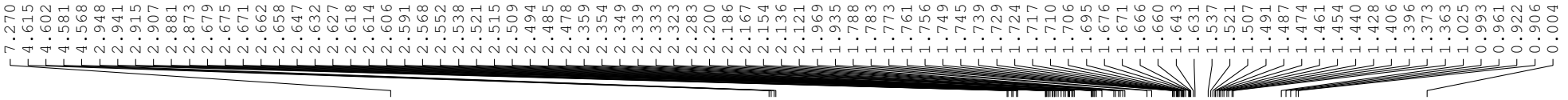
```
NAME      wwjdhma-06-79A-2
EXPNO                   11
PROCNO                   1
Date_             20150628
Time                 15.48
INSTRUM              spect
PROBHD    5 mm PABBO BB/
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                     256
DS                       2
SWH              24038.461 Hz
FIDRES            0.366798 Hz
AQ                1.3631988 sec
RG                    2050
DW                  20.800 usec
DE                   6.50 usec
TE                  296.1 K
D1               2.00000000 sec
D11              0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1           100.6228298 MHz
NUC1                    13C
P1                    12.00 usec
SI                    32768
SF             100.6127751 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```



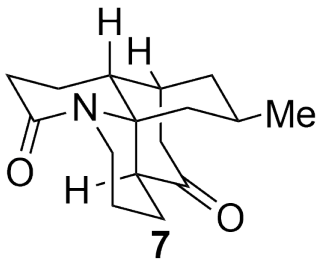

**16**

100 M, $CDCl_3$



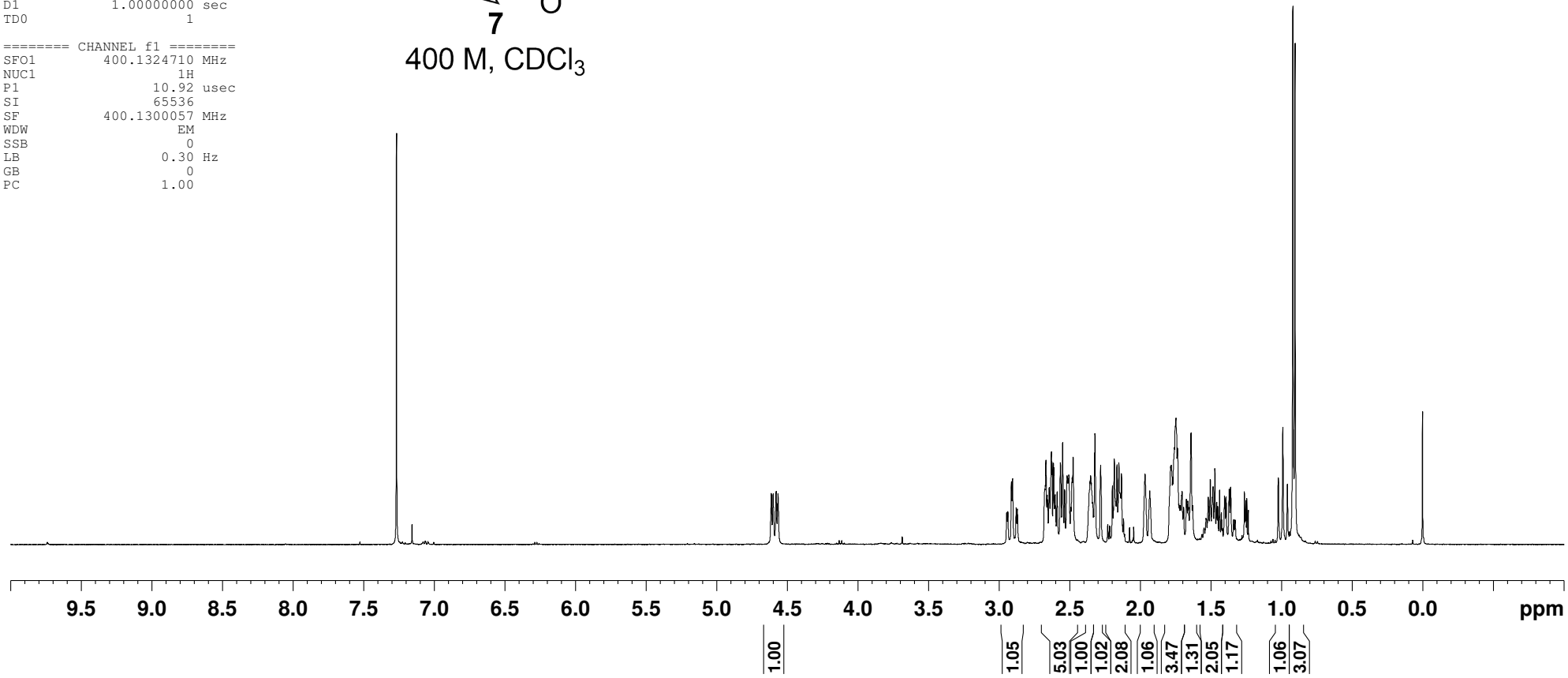


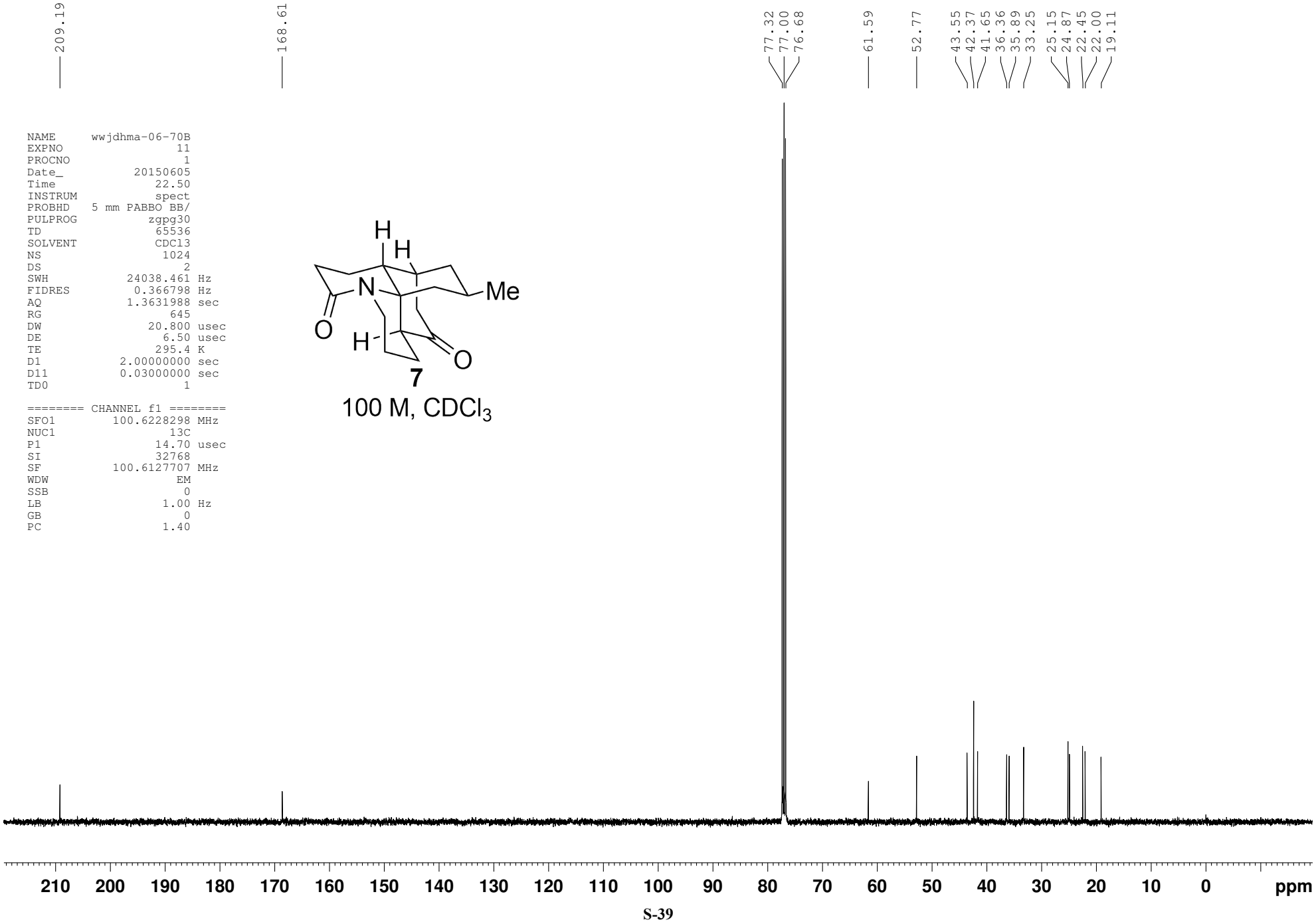

```
NAME      wwjdhma-06-70B
EXPNO                10
PROCNO                1
Date_          20150605
Time              22.01
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            8012.820 Hz
FIDRES            0.122266 Hz
AQ             4.0894966 sec
RG                  322
DW                62.400 usec
DE                 6.50 usec
TE                294.4 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1         400.1324710 MHz
NUC1                1H
P1                10.92 usec
SI                65536
SF           400.1300057 MHz
WDW                 EM
SSB                  0
LB                0.30 Hz
GB                   0
PC                1.00
```

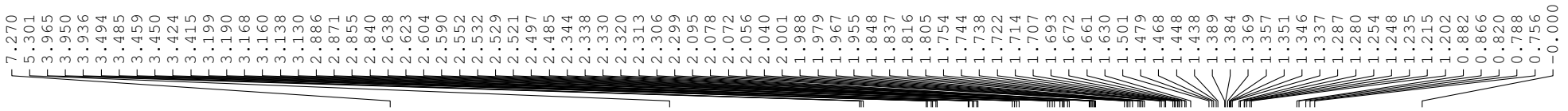



**7**

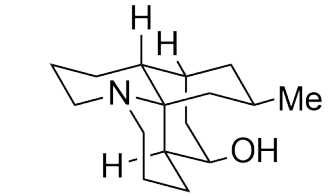
400 M, $CDCl_3$



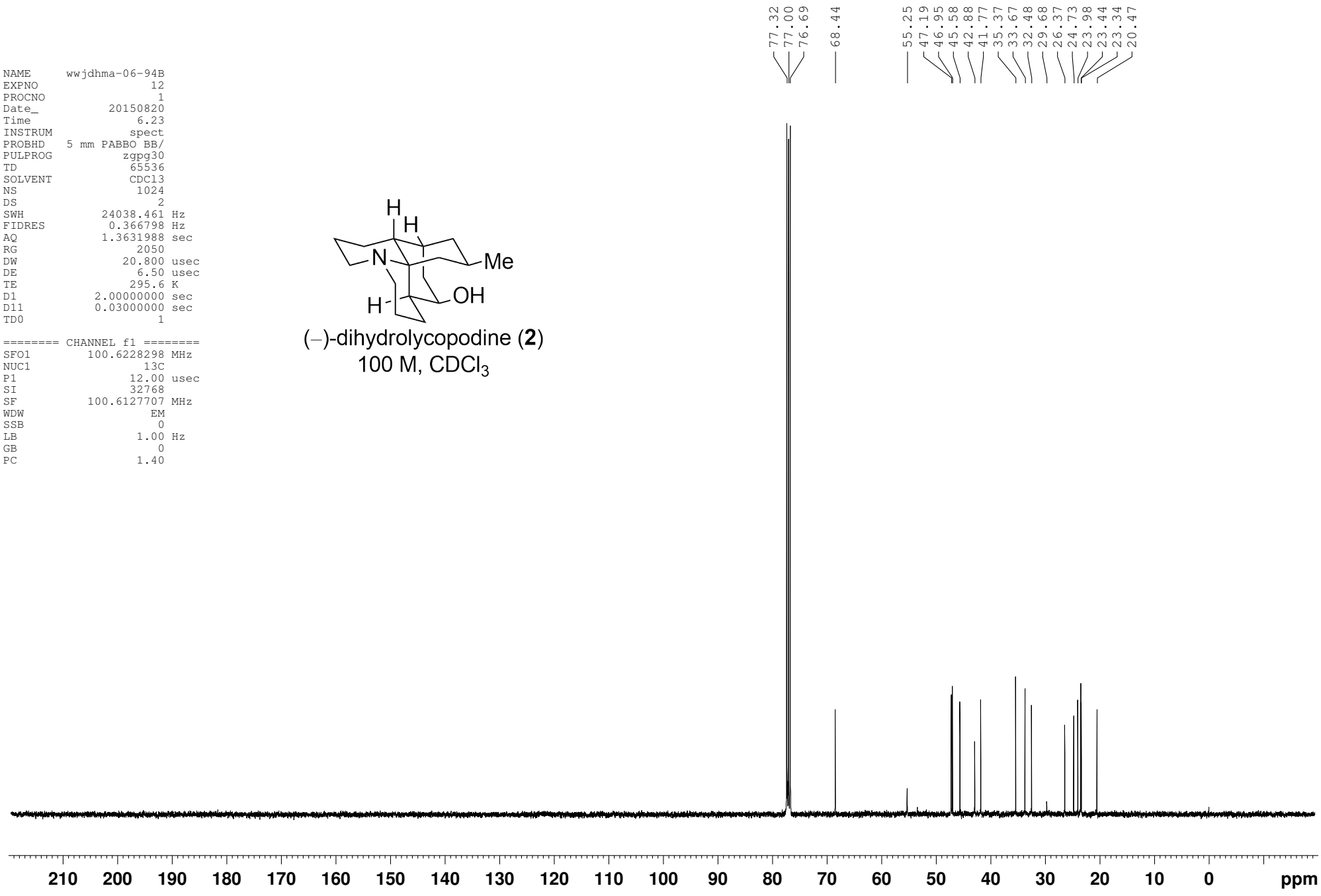

209.19
168.61
77.32
77.00
76.68
61.59
52.77
43.55
42.37
41.65
36.36
35.89
33.25
25.15
24.87
22.45
22.00
19.11
NAME wwjdhma-06-70B
EXPNO 11
PROCNO 1
Date_ 20150605
Time 22.50
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 2
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 645
DW 20.800 usec
DE 6.50 usec
TE 295.4 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 100.6228298 MHz
NUC1 13C
P1 14.70 usec
SI 32768
SF 100.6127707 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
H
H
N
Me
O
H
O
7
100 M, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

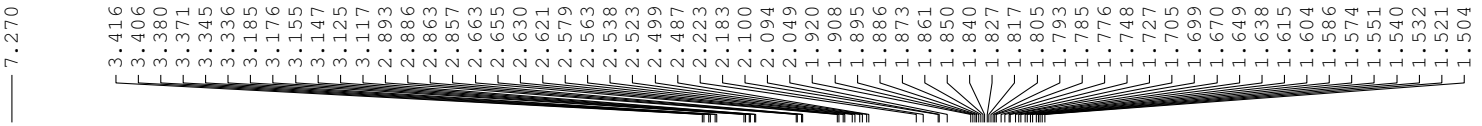



```
NAME      wwjdhma-06-94B
EXPNO                11
PROCNO                1
Date_          20150820
Time               5.23
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            8012.820 Hz
FIDRES         0.122266 Hz
AQ            4.0894966 sec
RG                  181
DW               62.400 usec
DE                6.50 usec
TE               294.4 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        400.1324710 MHz
NUC1                  1H
P1                10.79 usec
SI                65536
SF          400.1300057 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

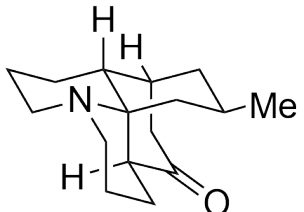



(−)-dihydrolycopodine (**2**)
400 M, $CDCl_3$

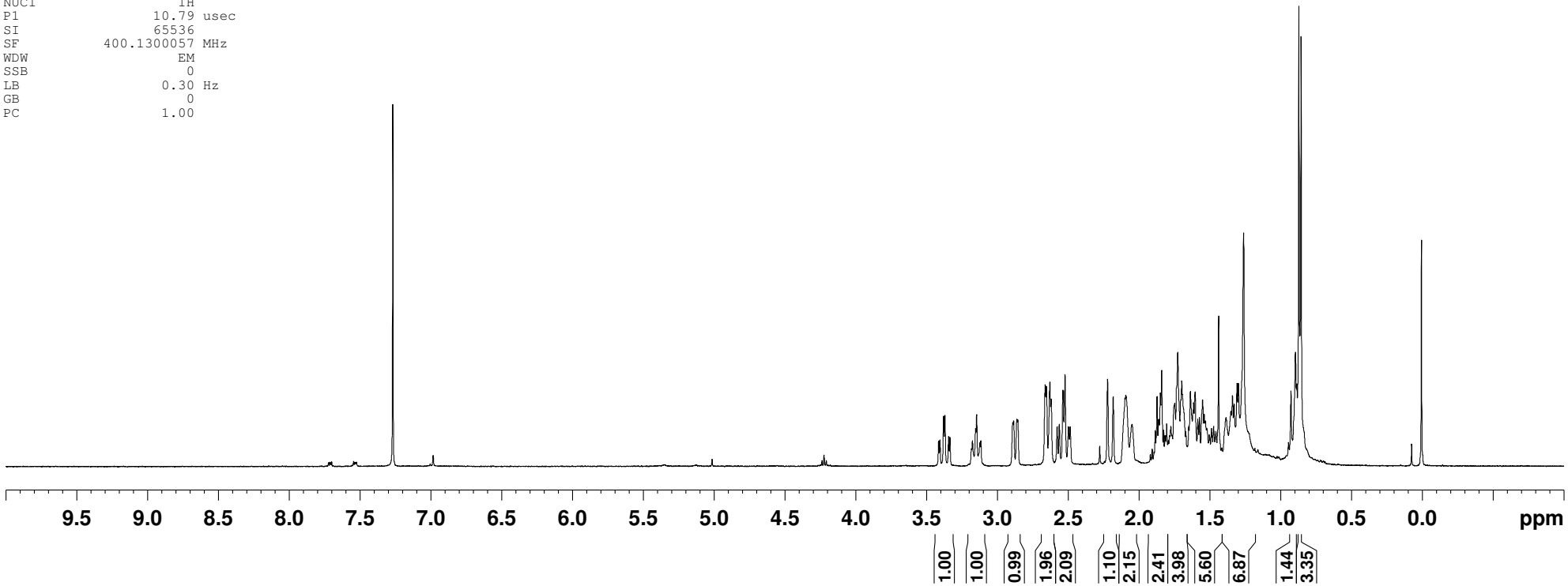

77.32
77.00
76.69
68.44
55.25
47.19
46.95
45.58
42.88
41.77
35.37
33.67
32.48
29.68
26.37
24.73
23.98
23.44
23.34
20.47
NAME wwjdhma-06-94B
EXPNO 12
PROCNO 1
Date_ 20150820
Time 6.23
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 2
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 2050
DW 20.800 usec
DE 6.50 usec
TE 295.6 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 100.6228298 MHz
NUC1 13C
P1 12.00 usec
SI 32768
SF 100.6127707 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
H
H
N
Me
OH
H
(–)-dihydrolycopodine (2)
100 M, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

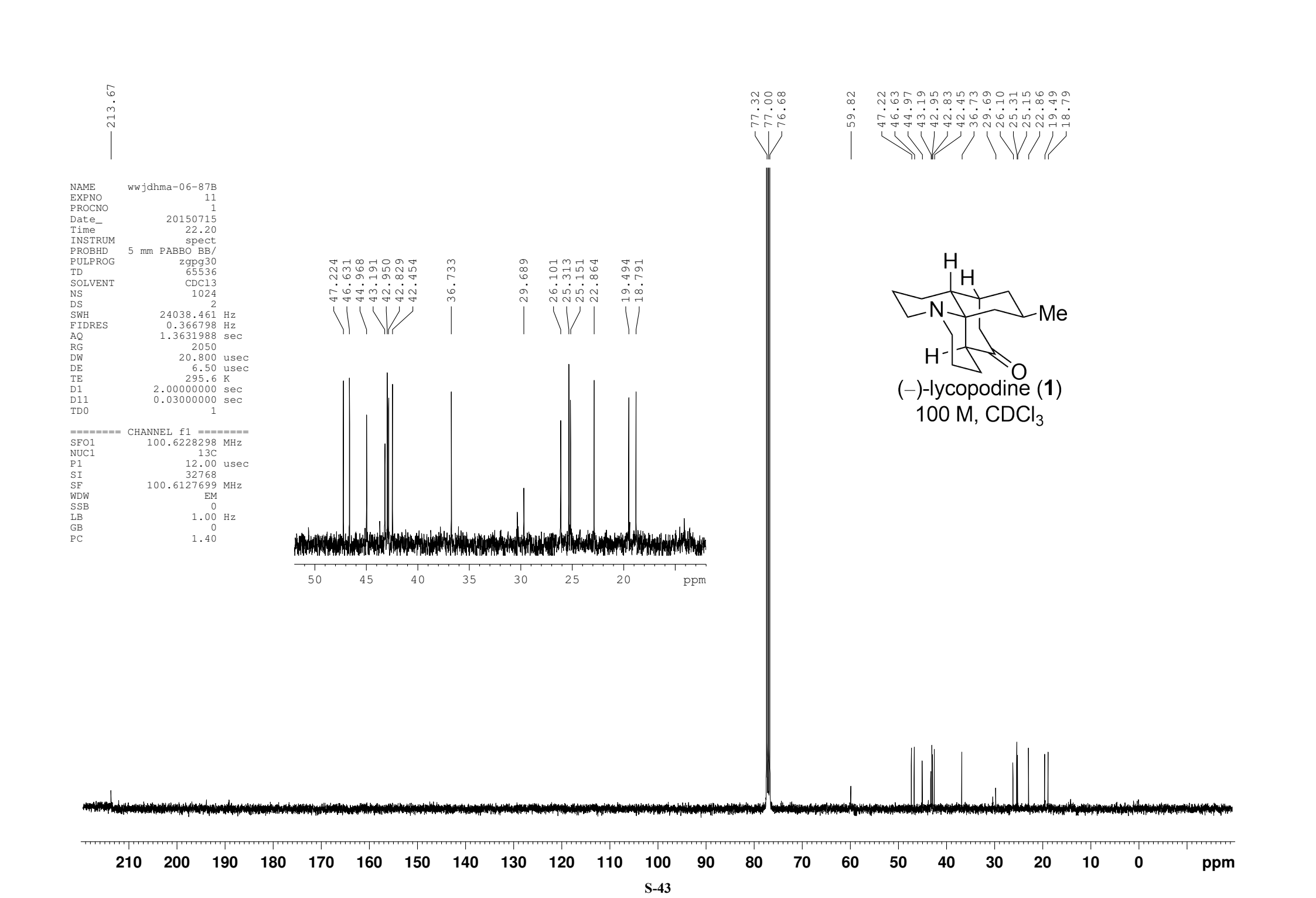



```
NAME      wwjdhma-06-87B
EXPNO                 10
PROCNO                 1
Date_           20150715
Time               22.05
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ              4.0894966 sec
RG                   287
DW                62.400 usec
DE                 6.50 usec
TE                294.5 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         400.1324710 MHz
NUC1                   1H
P1                 10.79 usec
SI                 65536
SF           400.1300057 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```




(–)-lycopodine (**1**)
400 M, $CDCl_3$




213.67
77.32
77.00
76.68
59.82
47.22
46.63
44.97
43.19
42.95
42.83
42.45
36.73
29.69
26.10
25.31
25.15
22.86
19.49
18.79
NAME wwjdhma-06-87B
EXPNO 11
PROCNO 1
Date_ 20150715
Time 22.20
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 2
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 2050
DW 20.800 usec
DE 6.50 usec
TE 295.6 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 100.6228298 MHz
NUC1 13C
P1 12.00 usec
SI 32768
SF 100.6127699 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
47.224
46.631
44.968
43.191
42.950
42.829
42.454
36.733
29.689
26.101
25.313
25.151
22.864
19.494
18.791
50
45
40
35
30
25
20
ppm
H
H
N
Me
H
O
(–)-lycopodine (1)
100 M, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm