NMR titration of *n-BuLi, t-BuLi, and MeLi.*

1. **Sample Preparation.**

a. The hydrocarbon reference (ca. 100 µL 1,5-cyclooctadiene) was added to a tared 5 mm NMRtube, and the mass of the standard was recorded. [Although the tube typically was flushed with nitrogen prior to adding the standard, this is not essential.]

b. A precise volume of the anion solution (500 µL, *e.g. n*-BuLi…) and C_6D_6 (150 µL, for making shimming easy) was added; the tube was capped with a standard plastic NMR tube cap (or septa-sealed cap NMR tube), and the tube was *agitated* to homogenize the solution.

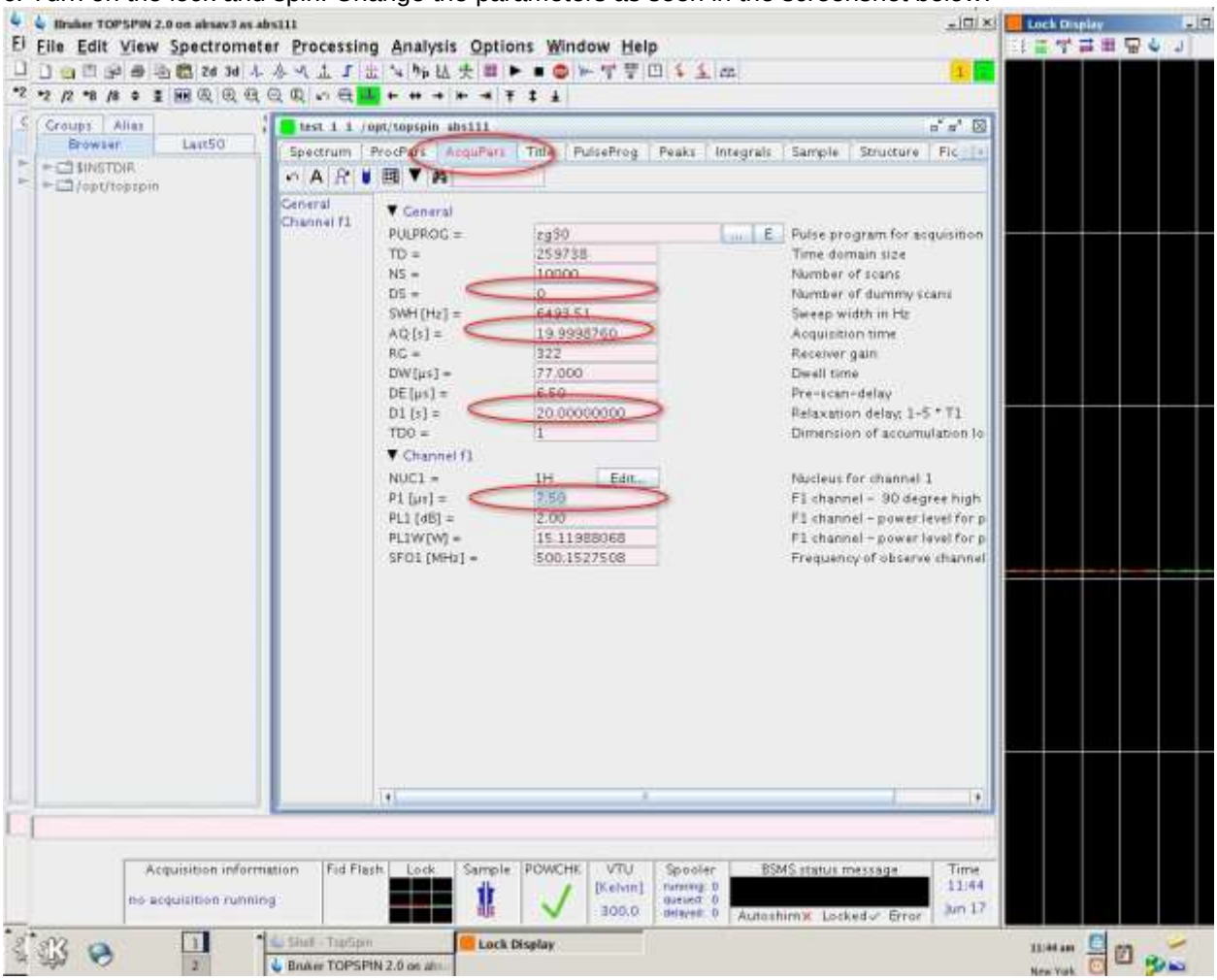
c. Shimming was performed as described in detail below.

2. **Data Acquisition.**

a. Go to the NMR lab and insert your sample.

b. Change the solvent to benzene (type “lopo” and select C_6D_6)

c. Turn on the lock and spin. Change the parameters as seen in the screenshot below.



For changing these parameters (eda), click **AcquPars** Tap; **DS** (dummy scan) **0**, **AT** (acquisition time) **20 s**, **D1**(delay time) **20 s**, and **P1 7.5 µs**, which are highlighted in the red ovals.]

d. Run topshim [type “ topshim gui’

e. Type “rga” and after the completion of rga, type “zg” (2-4 scans are enough)

d. Integrate resonances from anion and COD and calculate a concentration. See examples.

Example. Titration of MeLi

average 1.635 M of MeLi

ca. 100 μL (COD) = 90.2 mg = 0.833 mmol (COD) × $\frac{\frac{74.7 \text{ (integration of } CH_3Li \text{ at -1.9 ppm)}}{3 \text{ (number of protons of } CH_3Li \text{)}}}{\frac{100 \text{ (integration of vinyl protons of COD at 5.4 ppm)}}{4 \text{ (number of protons in vinyl protons of COD)}}}$

MW 108.18
d 0.882

= 0.830 mmol (MeLi) / 0.5 mL (volume of MeLi)

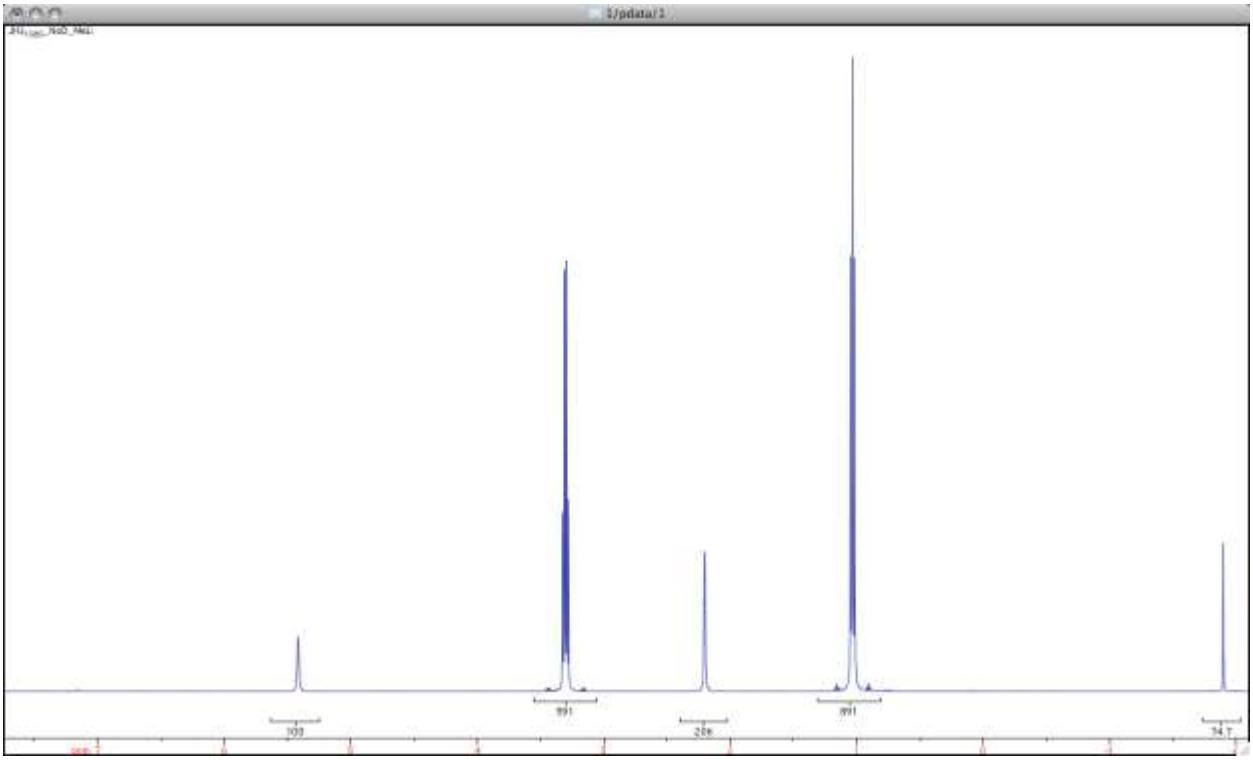
= 1.66 M (concentration of MeLi)

ca. 100 μL (COD) = 90.2 mg = 0.833 mmol (COD) × $\frac{\frac{74.7 \text{ (integration of } CH_3Li \text{ at -1.9 ppm)}}{3 \text{ (number of protons of } CH_3Li \text{)}}}{\frac{206 \text{ (integration of allylic protons of COD at 2.2 ppm)}}{8 \text{ (number of protons in allylic protons of COD)}}}$

MW 108.18
d 0.882

= 0.806 mmol (MeLi) / 0.5 mL (volume of MeLi)

= 1.61 M (concentration of MeLi)



Reference: Hoye, T.R.; Eklov, B. M.; Voloshin, M. *Org. Lett.* **2004**, *6*, 2567-2570 and also see the supporting information.